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The Thomas-Fermi Approximation in Quantum Mechanics

By N. H. MARCH
Department of Physics, The University, Sheffield

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§ 1. INTRODUCTION

THE Thomas–Fermi (TF) approximation, introduced originally as a means of calculating electron distributions and fields in heavy atoms (Thomas 1927, Fermi 1928), has proved to be of very considerable value in tackling many-body problems in quantum mechanics and by now has been applied to molecules, solids and nuclei. The nuclear applications will not be included in this review, but the interested reader may refer to Gombás (1952), where many earlier references are given.

In the present article a brief summary of the basic equations of the theory, together with the types of solution, will be given in §§ 2–4, while in § 5 recent work on atoms is discussed, with particular emphasis on the calculation of atomic binding energies. Section 6 is concerned with recent applications in molecular theory; especially with results which have been obtained for polyatomic molecules. Section 7 is devoted to solids; both perfect crystals and perturbed lattices being considered. It may be remarked here that at the present stage in the development of the theory of the perturbed lattice, the TF approximation provides a very useful approach to quite a number of important problems. A recent review by Friedel (1954) in this Journal, has been almost entirely devoted to this method of dealing with impurities in metals, but some developments since then are of considerable interest and will therefore be discussed here. Following this, the important work on solids under very high pressures, as found, for example, in stars, is considered at some length in § 8.

In addition to the detailed applications of the TF approximation referred to above and covered in §§ 5–8, a critical discussion of the various generalizations which have been proposed and of the fundamental basis of the method is given in § 9. It should be remarked at this stage that the one-electron approximation lies at the foundations of the TF theory (although an attempt has been made to include some account of correlation in the scheme (Gombás 1943, see, however, Fröman 1952) and that it therefore contains all the defects associated with the one-electron approach. In addition, other approximations are made which are essentially of a semi-classical nature, and thus it can only be expected in general that less accurate results will be obtained than with the Hartree or Hartree–Fock methods. The chief merit of the approach lies in the fact that in many problems which at present cannot be treated directly by the Hartree or Hartree–Fock methods because of mathematical complexities, the simplification brought about by the semi-classical approximations is such that the method remains entirely practicable. It is to be hoped that, in the future, general methods of correcting for the defects thereby introduced can be found, and some recent progress in this direction is reported in § 9.

Finally, only recent developments in the theory will of course be considered in this review. For the earlier work, the reader may make reference particularly to the valuable monograph of Gombás (1949). There is also an interesting chapter on the statistical theory in the book by Corson (1951) on many-body problems, and the pamphlet by Brillouin (1934 a), in spite of the fact that it was written more than twenty years ago, remains useful and stimulating.

§ 2. THE THOMAS–FERMI EQUATION

We begin by giving a simple derivation of the basic equations of the theory. We assume that we can deal with the electrons in the system we are considering, be it atom, molecule or crystal, as though they constitute a completely degenerate gas. Then the Fermi–Dirac statistics applied at the absolute zero of temperature tell us that we can put two electrons with opposed spins into each cell of phase space of volume h^3, filling up the momentum space until all the electrons are accommodated in the lowest momentum states. Suppose that around a point defined by the position vector $\mathbf{r}$, the momentum space is occupied up to a maximum momentum $p_0(\mathbf{r})$. Then the volume of occupied phase space corresponding to unit volume of ordinary space is

$$\tfrac{4}{3}\pi p_0^3(\mathbf{r})$$

and so the electron density, or number of electrons per unit volume at $\mathbf{r}$, say $n(\mathbf{r})$, is given by

$$n(\mathbf{r})=\frac{8\pi}{3h^3}p_0^3(\mathbf{r}). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2.1)$$

We now write down the classical energy equation for the fastest electron. This is

$$E_0=\frac{p_0^2(\mathbf{r})}{2m}-eV(\mathbf{r}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2.2)$$

where E_0 is the maximum occupied energy level and $V(\mathbf{r})$ is the electrostatic potential. Substituting for $p_0(\mathbf{r})$ from (2.2) in (2.1) and setting $E_0=-eV_0$ for convenience, we obtain

$$n(\mathbf{r})=\frac{8\pi}{3h^3}(2me)^{3/2}(V-V_0)^{3/2}, \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2.3)$$

the TF relation between the density n and the potential V. Obviously we may only use this when $V\geqslant V_0$; for $V<V_0$, n is zero in this approximation.

At this stage we invoke directly the requirement of self-consistency, namely that the electrostatic potential V shall be created by the electronic cloud of density n and the nuclei in the system under consideration. This is simply expressed in Poisson's equation

$$\nabla^2 V=-4\pi\rho=4\pi ne, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2.4)$$

ρ being the charge density. Thus, combining (2.3) and (2.4) we obtain the TF equation

$$\nabla^2(V-V_0)=\mu(V-V_0)^{3/2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2.5)$$

where

$$\mu=\frac{32\pi^2 e}{3h^3}(2me)^{3/2}.$$

Before going on it is of considerable importance to note that the fundamental relation (2.3) can be obtained from a variation principle. The total energy E in the present approximation may be written

$$\mathrm{E}=c_k\int n^{5/3}d\tau-e\int nV_N\,d\tau-\tfrac{1}{2}e\int nV_e\,d\tau+U_N \quad . \quad . \quad . \qquad (2.6)$$

where

$$c_k=\frac{3h^2}{10m}\left(\frac{3}{8\pi}\right)^{2/3},$$

V_N is the potential due to the nuclei and V_e that due to the electrons. The first integral represents the kinetic energy of the electrons, the second and third are the electronic potential energy terms due to electron–nuclear and electron–electron interactions respectively, and U_N is the nuclear–nuclear interaction energy. The requirement that E shall be stationary with respect to variations of the electron density n, subject to the condition that the total number of electrons shall remain constant, leads directly to (2.3); V_0 playing the role of the Lagrange multiplier introduced to take care of normalization. The energy eqn. (2.6) is most important in what follows, and furthermore we can make the variational derivation the basis for the introduction of exchange (Jensen 1934), which we shall now consider.

§ 3. INTRODUCTION OF EXCHANGE

Equation (2.1) is, of course, a consequence of applying free electron relations locally, and the kinetic energy term in (2.6) can be obtained immediately in this way by noting that the energy per unit volume of N free electrons enclosed in a volume V is

$$c_k\left(\frac{N}{V}\right)^{5/3}.$$

Now Bloch (1929) was the first to evaluate the exchange energy per unit volume for such a system of free electrons, and he obtained the result

$$-c_e\left(\frac{N}{V}\right)^{4/3}$$

where $c_e=\frac{1}{4}3e^2(3/\pi)^{1/3}$. We see then, by applying the free electron formula locally, that the exchange energy A in the TF theory may be written

$$A=-c_e\int n^{4/3}d\tau, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.1)$$

and adding this to the energy expression (2.6) gives the total energy including exchange. The requirement that this energy shall be stationary with respect to variations of the electron density n leads to the modified relation between density and potential

$$n=\frac{8\pi}{3h^3}(2me)^{3/2}\left[a+(V-V_0+a^2)^{1/2}\right]^3 \quad . \quad . \quad . \quad (3.2)$$

where $a=(2me^3)^{1/2}/h$. This is the Thomas–Fermi–Dirac (TFD) relation. We have kept here only the positive sign before the square root; there is in fact the possibility of a negative sign, but it will suffice to say that no physical application has so far been made using this alternative. For a discussion of this point, reference should be made to Plaskett(1953), where, in addition, the original proof of (3.2) (Dirac 1930) is criticized and a modified relation based on Slater's proposed simplification of the Hartree–Fock equations (Slater 1951) is suggested. However, the above derivation is quite consistent with the basic assumptions of the TF theory and whilst there is certainly much need for further clarification from a fundamental point of view, it is the opinion of the present writer that the TF relation with exchange given in (3.2) is to be preferred to the modified form. Finally, combining (3.2) with Poisson's equation we obtain a generalization of (2.5); the TFD equation.

§ 4. SOLUTIONS WITH SPHERICAL SYMMETRY

Throughout this review we shall deal most frequently with the original TF equation and only note important differences which occur when working with the TFD model. In all the applications where we assume spherical symmetry we will take it that there is a nucleus with charge Ze at the origin of coordinates. Thus, if r is the distance measured from the nucleus, the potential will approach Ze/r as r tends to zero, and it is convenient to put

$$V-V_0=\frac{Ze}{r}\phi, \quad r=bx \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.1)$$

where

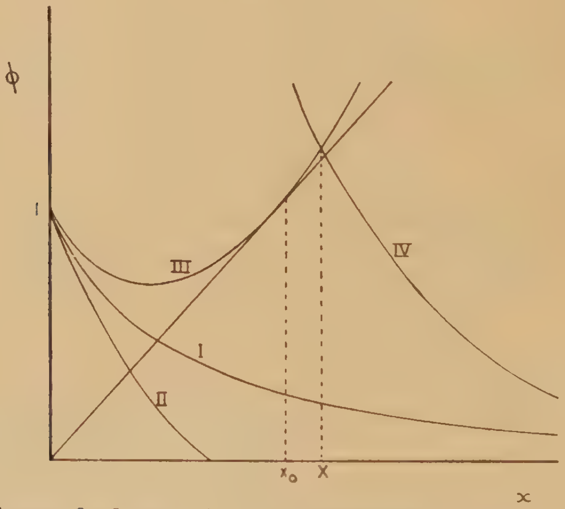
$$b=\left(\frac{3}{32\pi^2}\right)^{2/3}\frac{h^2}{2me^2Z^{1/3}}=\frac{0{\cdot}88534}{Z^{1/3}}a_0$$

and a_0 is the Bohr radius $h^2/4\pi^2me^2$. x and ϕ are then of course dimensionless and we shall refer to the resulting equation

$$d^2\phi/dx^2=\phi^{3/2}/x^{1/2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.2)$$

as the dimensionless TF equation.

Fig. 1



Types of solution of the dimensionless TF eqn. (4.2).

The types of solution of this equation for which $\phi(0)=1$ are shown in fig. 1. We shall briefly note their physical interpretation here, leaving the detailed discussion of the various cases over to the appropriate point in the review. The interpretation of the various solutions is as follows :

(i) Isolated atoms. At large distances $\phi\sim144x^{-3}$.

(ii) Positive ions. We shall say no more about these solutions, and we mention them at this stage for completeness.

(iii) Crystals, when the ' sphere approximation ' is made. To ensure charge neutrality we must cut off the solutions at the point x_0 at which a line passing through the origin is tangential to the curve. (For further details see Slater and Krutter 1935, also § 7.1).

(iii) and (iv) Molecules with high symmetry. The solution appropriate to describe molecules is given by (iii) out to a certain point X, and after that by (iv). The discontinuity in the slope at X corresponds to the electrostatic requirement that the field is discontinuous across a surface distribution of charge (see § 6.2).

The most important difference which arises when we are dealing with the dimensionless TFD equation

$$\frac{d^2\phi}{dx^2}=x\left[\alpha+\left(\frac{\phi}{x}\right)^{1/2}\right]^3 \quad \cdots\cdots \quad (4.3)$$

where

$$V-V_0+a^2=(Ze/r)\phi, \quad r=bx \quad \text{and} \quad \alpha=6^{1/3}/4(\pi Z)^{2/3},$$

concerns the solution of the form of (i). There is a solution of (4.3) which is tangential to the x-axis, but the point of tangency occurs at a finite value of x, and not at infinity, as with (i). Also $\phi=0$ does not now imply that the electron density is zero, and we have the state of affairs in which there is a discontinuity in the charge density at the boundary if we interpret this solution naively, and largely by analogy, as representing isolated atoms. It appears then that there is no satisfactory isolated atom in the TFD model (see especially March 1954 b). This difficulty has not yet been resolved, although the present writer has made a tentative suggestion which might lead to the way out of the difficulty if it could be investigated quantitatively. The standpoint taken is that the variation principle from which the Euler equation leading to (3.2) is derived is more general than (3.2). In fact, when (3.2) is combined with Poisson's equation the resulting differential equation does not possess solutions which can be interpreted physically as describing isolated atoms (although we shall see in § 7.1 that the solutions of the dimensionless TFD eqn. (4.3) satisfactorily represent crystals, within the framework of the sphere approximation), whereas the writer feels that the introduction of additional restrictive conditions into the variation principle could lead to a ' best ' density satisfying the physical conditions appropriate for isolated atoms. This ' best ' density would not lead to an absolute minimum in the energy (as discussed below this minimum is given by the solution of the TFD equation which Jensen interprets as describing isolated atoms) but to a minimum for densities which satisfy the additional restrictive conditions. These, it seems to the present writer, should enforce the continuity of the density, and preferably ensure that the density extends to infinity, although this latter condition is not essential provided normalization requirements are satisfied†.

---

† For example, the TF approximation applied to the Coulomb field problem leads to a satisfactory description in which the electron density is zero on a finite boundary.

Unfortunately, the problem of finding the 'best' density satisfying continuity requirements has proved intractable up to the moment. However, a fairly satisfactory way has been found of circumventing the difficulties mentioned here, by using the fact that a good energy can be obtained with a density which is not quite correct, the variational density chosen being such that the requirements of continuity and normalization are automatically satisfied.

In concluding this discussion of the difficulties of the TFD model, it is only fair to point out that there appears to be no universal agreement with regard to the position as stated above. Dirac (1930) in his original paper believed his modification of the TF method to be unsuitable to describe isolated atoms. Brillouin (1934 b), on the other hand, made the suggestion that the solution which is tangential to the x-axis† should be taken as the 'best' representation of the isolated atom. Slater and Krutter (1935) regarded this as quite unsatisfactory and proposed that this solution represented a crystal (see § 7.1). Jensen (1935) at the same time, and therefore unaware of the work of Slater and Krutter, proposed that the solution of the TFD equation which leads to an absolute minimum in the energy, and corresponds to a slightly smaller radius than Brillouin's 'atom', should be taken to represent isolated atoms. This solution can, however, be interpreted in a quite different and physically more satisfying manner (March 1954 b: see also § 7.1.1). Nevertheless, it is still true that many workers have adopted the model of Jensen (Gombás 1949, 1956, Bonet and Bushkovitch 1953, Thomas 1954, Sheldon 1955), and there seems at present to be no way of giving a definitive proof of the correctness of either viewpoint. In the opinion of the writer, however, the weight of evidence is heavily against the interpretation given by Jensen (1935).

We have discussed this difficulty at the present stage since it arises directly from the forms of solution of the dimensionless TFD equation. We shall now proceed to examine various physical consequences arising from the application of the TF theory to atoms, and exchange will be introduced in an approximate way which is consistent with the views expressed above.

§ 5. ATOMS

5.1. *Binding Energies*

Interest in the problem of calculating atomic binding energies has been revived recently by Foldy (1951), who examined how the calculations could be carried out from Hartree self-consistent field results. He showed that once the potential $V_e(0)$ at the nucleus due to the electrons is known, a relatively simple method based on Feynman's theorem (Feynman 1939) allows approximate binding energies to be obtained.

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† Tables of solutions satisfying this requirement and the usual condition $\phi(0)=1$ have been given for all elements by Umeda (1942).

A table of $V_e(0)$ had been constructed earlier by Dickinson (1950) in connection with the calculation of the internal diamagnetic field for atoms, and Foldy, using these results, found that the binding energies for large atomic number Z vary approximately as $Z^{12/5}$. This smooth dependence on atomic number prompted Scott (1952) to examine the reasons why the usual TF formula, due essentially to Milne (1927), is not in good agreement with experiment. We shall now consider this important contribution to the theory in some detail.

First of all, let us deal with the simplified case when we have Z non-interacting electrons moving in a Coulomb potential Z/r (atomic units will be used throughout this section). This will help us to understand the general features of the binding energy formula for atoms, as well as the limitations of the TF approximation. It will then, of course, be necessary to discuss the case of a proper self-consistent field in order to obtain quantitative results.

In the Coulomb field case the exact wave-mechanical solution is of course known and we consider this first. If we have N completed shells, the total energy E_c (simply the sum of the eigenvalues) is given by

$$\mathrm{E}_c = -\frac{Z^2}{2n^2}2n^2N, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5.1)$$

there being $2n^2$ electrons in the closed shell of principal quantum number n. We have also a relation between N and Z, namely that

$$\sum_1^N 2n^2 = Z$$

or

$$N(N+1)(2N+1) = 3Z. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5.2)$$

In principle (5.1) and (5.2) give the total energy as a function of Z. However, let us now deal with the case of large Z and develop an asymptotic expansion for N. From (5.2) it is then easily shown that

$$N = (\tfrac{3}{2})^{1/3}Z^{1/3} - \tfrac{1}{2} + \tfrac{1}{18}(\tfrac{3}{2})^{2/3}Z^{-1/3} + 0(Z^{-5/3}). \quad . \quad . \quad . \qquad (5.3)$$

Thus from (5.1) and (5.3) we obtain

$$\mathrm{E}_c = -(\tfrac{3}{2})^{1/3}Z^{7/3} + \tfrac{1}{2}Z^2 - \tfrac{1}{18}(\tfrac{3}{2})^{2/3}Z^{5/3} + 0(Z^{1/3}). \quad . \quad . \qquad (5.4)$$

At this stage we apply the TF approximation to the same problem. There is no self-consistent field problem to solve, and so the density n is given immediately in this case by (2.3), with $V = Z/r$ and with V_0 chosen so that the total number of electrons is Z. Substituting this in the energy expression (2.6), remembering that $V_e = 0$, and performing the elementary integrations we find

$$\mathrm{E}_{c,\,\mathrm{TF}} = -(\tfrac{3}{2})^{1/3}Z^{7/3} = -1{\cdot}145Z^{7/3}. \quad . \quad . \quad . \quad . \qquad (5.5)$$

Comparison of (5.4) and (5.5) shows that the TF approximation is leading to the correct result only in the limit $Z \to \infty$, as is to be expected from the nature of the method. The leading term in the energy is $0(Z^{7/3})$; this is also the case for a proper self-consistent field (Milne 1927) with which we shall now deal.

We obtain the TF approximation to the energy by substituting in (2.6) the density n found from solution (i) of fig. 1. As Milne showed, once the solution (i) is known, no further quadrature is required to obtain the energy, and the result is

$$E_{TF}=-0{\cdot}7687Z^{7/3}. \qquad \text{(5.6)}$$

This energy is of course much higher than that for electrons moving in a pure Coulomb field, cf. (5.5), since the outer electrons in an atom are screened from the full effect of the nucleus by the inner shells, But, by analogy with the Coulomb field case, it is clear that (5.6) can be giving no more than the first term in an asymptotic expansion of the energy E in a series in $Z^{1/3}$, and we wish, therefore, to correct the TF formula, which has long been known to lead to energies which are much too low, by adding further terms.

Scott (1952) was the first to suggest how this could be done. He introduced two corrections, the first due to the so-called ‘ boundary effect ’, and the second due to exchange. The first correction is necessary because of the fact that the TF approximation is breaking down near the nucleus where the potential is varying rapidly. Scott argued that we can correct for this by calculating the difference between the TF and the exact results for the Coulomb field case, the justification being that, as he showed, the bulk of his correction term, $\frac{1}{2}Z^2$ (see eqn. 5.4 and the remarks made below), arises from the K shell†, where the Coulomb field approximation will be valid. Beyond this it seems difficult to give a completely clearcut demonstration of the case for including $\frac{1}{2}Z^2$, though several arguments (see especially the original derivation of Scott 1952 and the detailed analysis of the errors in the Coulomb field case given by March and Plaskett 1956) which we shall not go into here make it seem entirely plausible. Scott's argument was put rather differently from that given above; eqn. (5.4) was first obtained by Ballinger and March (1955 a) and shows that in the Coulomb field case there is also a term of $0(Z^{5/3})$ arising from errors in the TF approximation, whereas this term did not appear in Scott's original argument due to his procedure of taking the limit as the number of completed shells N tends to infinity. We shall now see that the term arising from exchange effects is also of $0(Z^{5/3})$.

As discussed earlier, when we are dealing with a system of interacting electrons we must take account of the exchange energy A and this is given in terms of the electron density n by eqn. (3.1). In view of the difficulties of the TFD model, Scott suggested that the original TF density be used as a variational function to calculate the total energy including exchange with small error; this density of course satisfies both the continuity and normalization requirements referred to in § 4. In this way he found by numerical integration the result

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† Scott's orginal argument gave $0{\cdot}44Z^2$ as the contribution to $\frac{1}{2}Z^2$ from the K shell. A somewhat different approach (March and Plaskett 1956) gives $0{\cdot}39Z^2$.

$$A = -0{\cdot}221Z^{5/3}. \qquad (5.7)$$

Scott thus obtained for the binding energy formula

$$-0{\cdot}7687Z^{7/3} + \tfrac{1}{2}Z^2 - 0{\cdot}221Z^{5/3} + 0(Z^{4/3}).$$

If, however, we adopt for the boundary correction the Coulomb field value obtained by taking the difference between eqns. (5.4) and (5.5), then the term in $Z^{5/3}$ becomes

$$-0{\cdot}294Z^{5/3}.$$

Recently a more fundamental investigation by March and Plaskett (1956) has shown that the correct result for this term lies between these two results and the value they propose leads to the formula

$$-0{\cdot}7687Z^{7/3} + \tfrac{1}{2}Z^2 - 0{\cdot}266Z^{5/3} + 0(Z^{4/3}). \qquad (5.8)$$

The method they employed will be referred to again in § 9.4.3 ; for the moment it will be sufficient to say that an attempt was made to carry through a similar argument to that outlined above for the Coulomb field, for the proper screened potential of the TF theory for atoms ; the difficulty is that the eigenvalues for this potential must be computed numerically (actually by the WKB method which, it should be noted, gives the exact eigenvalues for a Coulomb potential).

Table 1. Atomic Binding Energies (non-relativistic)

Z	6	9	13	18	23
‘ Observed ’	37·8	99·7	242·4	528	945
Eqn. (5.8)	37·6	99·4	240·1	524	941

In Table 1 we show the results obtained from (5.8) for a number of atoms, along with the ‘ observed values ’ given by Scott. These were calculated in such a way that they are non-relativistic, as, of course, are all our formulae. For further details of the way in which they were obtained, reference should be made to Scott's paper. It will be seen that the agreement between the calculated and ‘ observed ’ values is very remarkable ; much better than could really be expected from the nature of the formula (5.8). It seems relevant in this connection, however, to note that in the Coulomb field case, as (5.4) shows, terms of order $Z^{4/3}$, Z and $Z^{2/3}$ are missing, the first ‘ neglected ’ term being of order $Z^{1/3}$. Whilst this will certainly not be exactly the case with the formula (5.8), it seems very reasonable to suppose that the corresponding terms will be small, and that (5.8) will be a good approximation even for quite small Z.

In concluding this discussion, it should be mentioned that for any direct comparison with experiment to be possible, the relativistic correction to be applied to the binding energy formula must be known. Scott has made some rough estimates of this, and finds that his results can be represented approximately by the expression

$$|\mathrm{E}|_{\text{rel.}}-|\mathrm{E}|_{\text{non-rel.}}=4\times 10^{-6}Z^{9/2}. \quad . \quad . \quad . \quad . \quad (5.9)$$

Gilvarry (1954 a) has recently developed a new relativistic TF model (for further details see § 9.5), which may well avoid the difficulties associated with previous formulations. He has announced, but not yet published, an application of his model to obtain a more accurate estimate than (5.9) of the correction to the binding energy formula arising from relativistic effects.

5.2. *Modification of the TF Charge Distribution*

One further point arising from the previous considerations is worth discussing, namely that some account of exchange can be introduced into the density in a very simple way (March 1953 b). We start from Scott's suggestion that we can use the TF density (which we call $n_1(r)$ for the purpose of the present argument) as a variation function. This then suggests the use of the more general function

$$n_\lambda(r)=\lambda^3 n_1(\lambda r) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.10)$$

where λ^3 is introduced for normalization purposes. Such a scale factor was first introduced by Fock (1932) as a device to prove the virial theorem in the TF theory, and was subsequently put equal to unity. Here we use λ as a proper variational parameter. It is then very easy to show that

$$\mathrm{E}_\lambda=\lambda^2 T_1+\lambda U_1+\lambda A_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.11)$$

where T_1, U_1 and A_1 are respectively the kinetic, potential and exchange energies calculated using the unmodified density $n_1(r)$. Hence the value of λ, say Λ, which makes E_λ a minimum is given by

$$\Lambda=-(U_1+A_1)/2T_1. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.12)$$

The work of Milne, Baker (1930) and Scott enables us to write

$$\begin{aligned} \mathrm{E}_1&=-\beta Z^{7/3}, & U_1&=-2\beta Z^{7/3} \\ T_1&=\ \ \beta Z^{7/3}, & A_1&=-\gamma Z^{5/3} \end{aligned} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.13)$$

where $\beta=0{\cdot}7687$, $\gamma=0{\cdot}2208$ (both in atomic units) and $\mathrm{E}_1=T_1+U_1$. Hence we obtain

$$\left.\begin{aligned} \Lambda&=1+(\gamma/2\beta)Z^{-2/3} \\ &=1+0{\cdot}1436Z^{-2/3} \end{aligned}\right\}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.14)$$

Equation (5.10), with λ given by the value (5.14), defines a new charge distribution in which some account is taken of exchange. We see that the effect of exchange becomes smaller as Z increases, the improved charge distribution going over into the unmodified distribution as Z becomes very large. In order to illustrate the effect of Λ we show in fig. 2 the radial charge distribution $D(r)(=4\pi r^2 n(r))$ for the argon atom. The contraction of the charge cloud (and hence the lowering of the energy) is well shown. For large r, curve 2 of course falls below curve 1.

Finally it is worthwhile to examine the separate expressions for kinetic, potential and exchange energies. These are given by

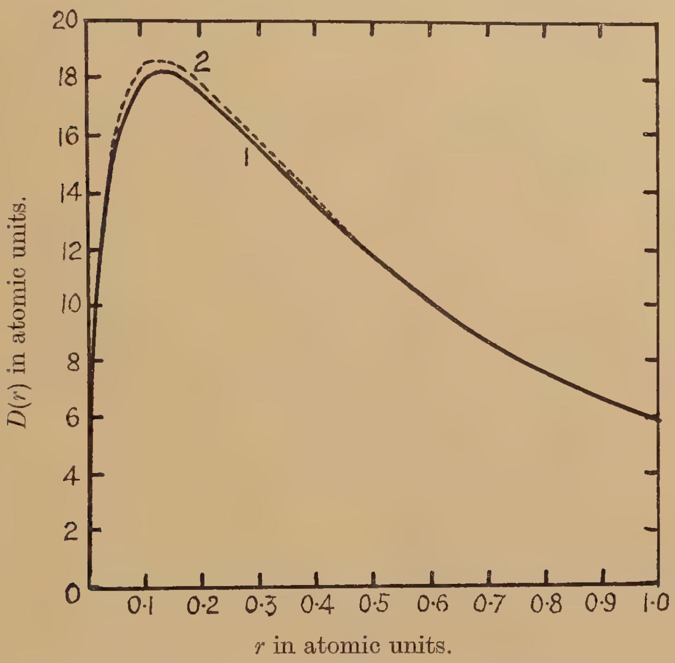
$$\left.\begin{aligned} T_A &= \beta Z^{7/3} + \gamma Z^{5/3} + (\gamma^2/4\beta)Z \\ U_A &= -2\beta Z^{7/3} - \gamma Z^{5/3} \\ A_A &= -\gamma Z^{5/3} - (\gamma^2/2\beta)Z \end{aligned}\right\} \quad . \quad . \quad . \quad . \qquad (5.15)$$

Adding these we have for the total energy

$$E_A = -\beta Z^{7/3} - \gamma Z^{5/3} - (\gamma^2/4\beta)Z, \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5.16)$$

which agrees with Scott's result (ignoring the boundary correction, of course) apart from the term in Z. The effect of introducing exchange into the density is therefore to change the kinetic and potential energies by terms of order $Z^{5/3}$, but these terms cancel in the total energy, and Scott's results are effectively regained. Also, it is worth noting from (5.15) that

Fig. 2



Radial charge distribution $D(r)$ for argon.
(1) Without exchange. (2) With exchange. (From March 1953 b.)

$$2T_A + U_A + A_A = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5.17)$$

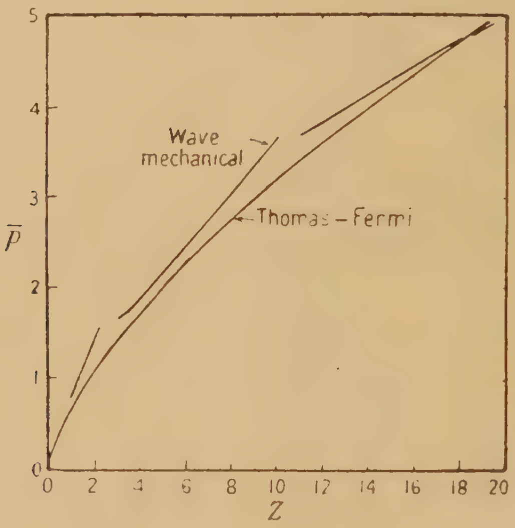
and hence the virial theorem is satisfied in this approximation, whereas it does not hold when λ is put equal to 1. (For a general discussion of the virial theorem in the TF theory, applicable to atoms, ions, molecules or crystals, see March 1952 b.)

5.3. *Linear and Angular Momentum Distributions*

In this section we shall briefly summarize two further applications of the theory which have been considered recently, the determination of linear and angular momentum distributions of electrons in atoms. In both these applications we shall restrict ourselves to a consideration of the results of the unmodified TF theory.

Coulson and March (1950) investigated the linear momentum distribution in detail in order to ascertain whether the theory is capable of providing useful results for heavy atoms (see also related work by Kónya 1949), thereby supplementing wave-mechanical results which have been obtained for atoms up to and including K. (For a useful summary of this latter work, due largely to Coulson and Duncanson, see the book by Sneddon 1951). The importance of the momentum distribution lies in the fact that it determines the shape of the Compton profile in x-ray scattering (Dumond 1933). The results were rather disappointing, however, for although a useful description of the momentum distribution function $I(p)$ (defined such that $I(p)dp$ is the probability of finding an electron with momentum of magnitude between p and $p+dp$) was afforded by the method, and the mean momentum, $\bar{p}$ (defined by $\bar{p}=\int_0^\infty pI(p)dp$) varies as $Z^{2/3}$ and is in reasonable agreement with wave mechanical calculations (see fig. 3), the Compton profile is of quite the wrong shape. The cause of this can be traced to the fact that the density in the TF atom decreases much too slowly at large distances; in fact as r^{-6} instead of exponentially. In view of this, we shall not elaborate here on the method of calculating electronic momentum distributions,

Fig. 3

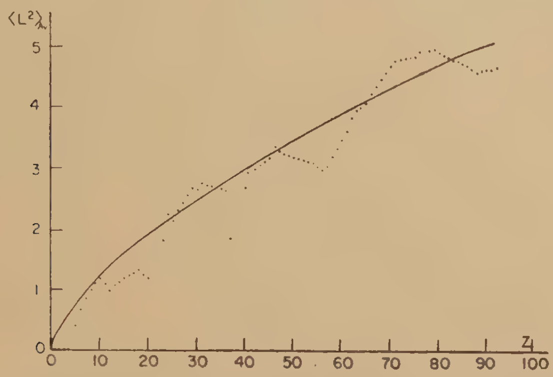


Mean momentum $\bar{p}$ as a function of atomic number.
(From Coulson and March 1950.)

but shall defer further discussion to § 7.1.2, where we shall see that for metals the method is capable of giving much better results.

Closely related to this work is the discussion of the angular momentum distribution in atoms. This was considered by Fermi in his original paper, and more recently by Jensen and Luttinger (1952) together with a treatment of the angular momentum distribution in the nucleus, which is, however, outside the scope of this review. These latter authors conclude that if attention is directed to a well defined quantity, the mean value of the square of the orbital angular momentum, $\langle L^2\rangle_{\text{Av}}$ say, then the results calculated from the TF theory agree quite well with the empirical values, as shown in fig. 4. However, they point out that previous calculations of the 'first appearance' of an electron with a given orbital angular momentum are rather arbitrary and that too much significance is not to be attached to them†. Certainly there seems very little justification for the procedure, often used in the past, of correlating the 'first appearance' of an electron with a given orbital angular momentum with the closing of a shell. This can be seen from the fact that the closed shells for atoms occur at $Z=2$, 10, 18, 36, 54 and 86, whilst the 'first appearance' of electrons with $l=1$, 2 and 3 occurs at $Z=5$, 21 and 58 respectively‡.

Fig. 4



Mean value of square of orbital angular momentum as a function of atomic number.
Solid line—results of TF theory.
Dotted line—empirical results.
(From Jensen and Luttinger 1952.)

5.4. *Atoms with Non-Zero Total Angular Momentum*

Following this brief discussion of the angular momentum distribution in the TF atom, it is appropriate to consider some recent work by Sessler and Foley (1954) on the generalization of the TF theory to deal with atoms which have a non-zero total angular momentum. Their main interests were to obtain estimates of the magnetic field at the nucleus due to the orbital motion of the electrons and the quadrupole coupling constant (see, for example, Ramsey 1953). The first quantity, as we shall see, is given sensibly by their method, but the second is the wrong order of magnitude. Atomic units are used below unless otherwise stated.

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† See, however, a recent paper by Theis (1955 a) in this connection.

‡ *Note added in proof.*—Some work on angular momentum distributions in the TFD model has recently been reported (Oliphant, T. A., 1956, *Phys. Rev.*, **104**, 954).

The variation principle for the total energy is made the basis of the work, but an additional restrictive condition is now imposed, namely that the total angular momentum shall be a non-zero constant. In order to have a resultant angular momentum about the origin, the electrons at a point defined by position vector $\mathbf{r}$ in coordinate space must have some net linear momentum, and Sessler and Foley consider the usual spherical distribution in momentum space to be displaced by an amount $\mathbf{D}$, dependent on $\mathbf{r}$. The total energy is now increased, because of the increase in kinetic energy arising from the linear momentum, and if $p_0(\mathbf{r})$ is the radius of the occupied sphere in momentum space, then it is easily shown that the total kinetic energy is

$$\int\left(\frac{{p_0}^5}{10\pi^2}+\frac{{p_0}^3D^2}{6\pi^2}\right)d\tau.$$

The angular momentum is now treated classically and J_z is taken equal to J. We have then for the total angular momentum

$$\mathbf{J}=\int \mathbf{r}\times\mathbf{D}(\mathbf{r})n(\mathbf{r})d\tau$$

and introducing spherical polar coordinates r, θ, ϕ we can write

$$J=\int D(\mathbf{r})r\sin\theta\, n(\mathbf{r})d\tau.$$

The potential energy is written down in the usual way and we must now minimize the total energy subject to the two conditions that the total number of electrons and the total angular momentum are constants. Introducing two Lagrange multipliers, λ and μ, and carrying through the variations with respect to D and n the following results are obtained :

$$\left.\begin{aligned}&D(\mathbf{r})=\lambda r\sin\theta\\ \text{and}\quad&\\ &\frac{5}{3}\frac{(3\pi^2)^{5/3}n^{2/3}}{10\pi^2}-\frac{\lambda^2r^2\sin^2\theta}{2}-V+\mu=0\end{aligned}\right\}\quad . \quad . \quad (5.18)$$

The equation for the density is easily seen to reduce to the customary TF relation (2.3) when $\lambda=0$. Using Poisson's equation, we have

$$\nabla^2(V-\mu)=\frac{4}{3\pi}\{2(V-\mu)+\lambda^2r^2\sin^2\theta\}^{3/2}, \quad . \quad . \quad (5.19)$$

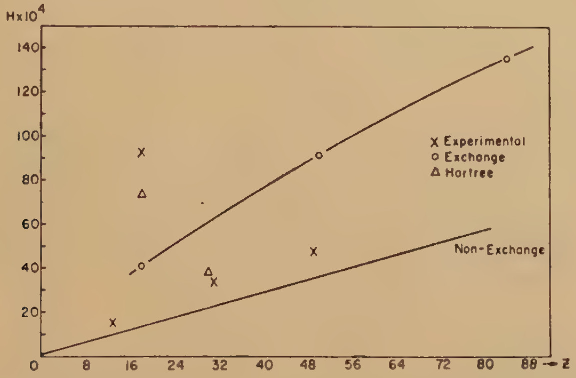
a generalization of the TF equation applicable when there is a net total angular momentum.

Sessler and Foley were interested in P states, for which J is unity, and thus λ small. Equation (5.19) was therefore solved by a perturbation method, for details of which the reader is referred to the original paper. It then turns out that the magnetic field at the nucleus due to the orbital motion of the electrons may be expressed to sufficient accuracy in terms of the unperturbed density (the familiar TF density), and the result may be written

$$H = 0{\cdot}73 \times 10^4 ZJ \text{ gauss.}$$

Calculations were also made to investigate the effect of exchange and it seems possible that this may be quite large. However, Jensen's interpretation of the isolated atom with exchange was adopted and it may be therefore that the quantitative results showing the effect of exchange should be treated with some reserve. The final results of the calculations are shown in fig. 5, together with the experimental values, and it can be seen how the TF statistical method averages the effect of shell structure.

Fig. 5



Magnetic field at the nucleus, due to orbital motion of electrons, as a function of atomic number.
(From Sessler and Foley 1954.)

The second quantity of interest that can be calculated from the present scheme is the quadrupole coupling constant q, given by

$$q = \int \frac{P_2(\cos\theta) n(\mathbf{r}) d\tau}{r^3} .$$

In the statistical treatment it turns out that this integral is weakly divergent for large r, but using a cut-off procedure Sessler and Foley find that a rough estimate of q is given by

$$q = -0{\cdot}002 J^2 / Z^{2/3}.$$

Due to the fact that the present model is not properly describing the charge distribution associated with quantum-mechanical angular momentum, it is not surprising that this formula is found to give values of q which are much too small.

5.5. *Eigenvalues for Statistical Potentials*

A number of workers have used statistical potentials as a basis for the determination of atomic eigenvalues. The most complete calculation of this kind has been carried out by Latter (1955 a), following earlier work by Rasetti (1928 a, b), Mayer (1941) and Gáspár (1952). Related work by Kerner (1951) and Tietz (1956) should also be mentioned here.

In Latter's work, which we shall consider in some detail, the TF and TFD results have been modified so that at large distances the fields tend to that of a unit charge. Some account is thus taken of the fact that in the original treatment (see § 2) each electron is assumed to move in its own field as well as that of the other electrons. Explicitly, the potential used for the TF case may be written,

$$\left.\begin{aligned} V(r) &= \frac{Ze}{r}\phi(x) \quad \text{if} \quad V(r) > \frac{e}{r} \\ &= \frac{e}{r}\,\text{otherwise} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (5.20)$$

It will be noted that no modification of the field for self-interaction has been made in the interior of the atom, but over most of this region it seems that this should be relatively unimportant. For comparison with (5.20) it is worth noting that Mayer used the potential

$$V(r) = \frac{(Z-1)e}{r}\phi(x) + \frac{e}{r} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.21)$$

to discuss the behaviour of 4f and 5f electrons ; Latter believes this to 'over-correct' for self-interaction. The function $\phi(x)$ for the isolated TF atom was approximated by the analytical form

$$\phi(x) = \left[\begin{matrix} 1 + 0{\cdot}02747x^{1/2} + 1{\cdot}243x - 0{\cdot}1486x^{3/2} + 0{\cdot}2302x^{2} \\ + 0{\cdot}007298x^{5/2} + 0{\cdot}006944x^{3} \end{matrix}\right]^{-1} \quad . \quad (5.22)$$

in Latter's calculations, the maximum error in this being less than 0·3%.

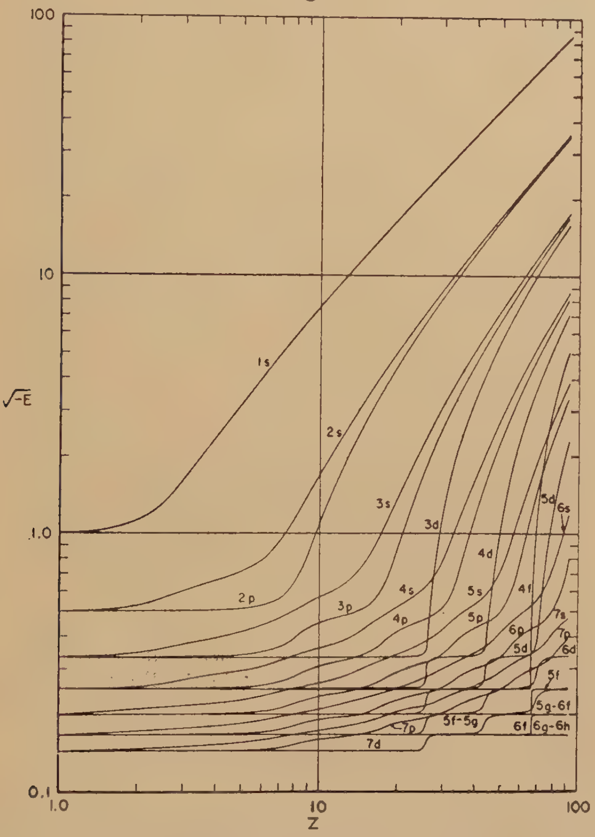
For the potential (5.20), with $\phi(x)$ given by (5.22), Latter has constructed an extensive table of term values from 1s to 7d, for a range of values of the atomic number Z sufficient to permit easy interpolation. For the precise numerical data, reference can be made to this table, but an indication of the main features of Latter's findings is given by fig. 6, taken from Latter's paper, where the square roots of the term values are plotted against Z.

Figure 7 shows similar results obtained using an approximate representation of the TFD potentials. As a basis, Latter adopted the isolated atom solutions proposed by Jensen (1935) ; these will doubtless give a rather better approximation to the potential in the interior of the atom, although, as discussed earlier, we believe the results to be unrealistic near the boundary. But, in any case, Latter modifies the potentials to have the asymptotic form appropriate to a unit charge, and adopts a universal potential given by

$$\left.\begin{aligned} V_{ex}(r) &= \frac{Ze}{r}\phi(x) + \frac{3e}{4\pi}\left(\frac{2Z}{a_0}\right)^{1/2}\left(\frac{\phi(x)}{r}\right)^{1/2} \quad \text{for} \quad V_{ex}(r) > \frac{e}{r} \\ &= \frac{e}{r} \text{ otherwise} \end{aligned}\right\}, \qquad (5.23)$$

where $\phi(x)$ is defined by (5.22). Latter found that such a potential deviated from the TFD potentials by less than 5% for $5<Z<92$, and (5.23) was used to draw up a further extensive table of eigenvalues.

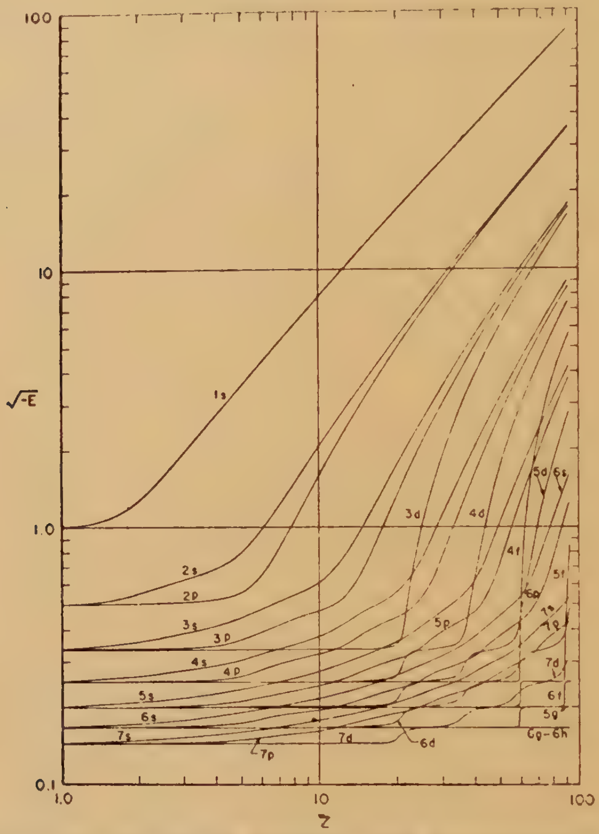
Fig. 6



The square root of the term values calculated with the modified TF potential (5.20), as a function of atomic number. Energies are measured in Rydbergs. (From Latter 1955 a.)

Finally a comparison of these results with Hartree and Hartree–Fock calculations and experimental ionization energies is shown in fig. 8 for s levels and in fig. 9 for p levels. Similar results for d and f levels are given by Latter but will not be reproduced here. For large Z, it is clear that relativistic effects become important (cf. eqn. (5.9)) and discrepancies exist between observed and calculated term values.†

Fig. 7



The square root of the term values calculated with the modified TFD potential (5.23), as a function of atomic number. Energies are measured in Rydbergs. (From Latter 1955 a.)

In concluding this summary of Latter's investigations, it may be remarked that a very useful overall picture of atomic behaviour is thus provided, whereas numerical labour makes it difficult to achieve this using Hartree or Hartree–Fock methods. The energies obtained from the TF or TFD potentials agree in general with experimental ionization energies as well as Hartree or Hartree–Fock results and thus seem to indicate that such statistical fields are of sufficient accuracy to be of considerable value.

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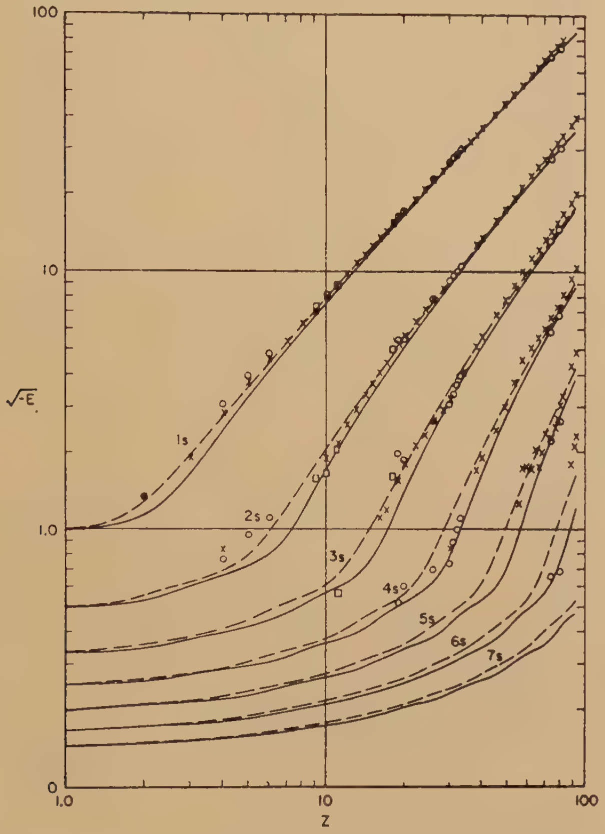
† Dr. R. Latter (private communication) has recently informed the writer that he has now calculated energy levels with the statistical potentials, but using Dirac's relativistic wave equation instead of Schrödinger's equation. He finds that the results for large Z are then improved appreciably.

5.6. *Analytical Approximations to the TF Solution for Isolated Atoms*

Finally, a number of workers have recently proposed analytical approximations to the TF solution for isolated atoms shown in curve I

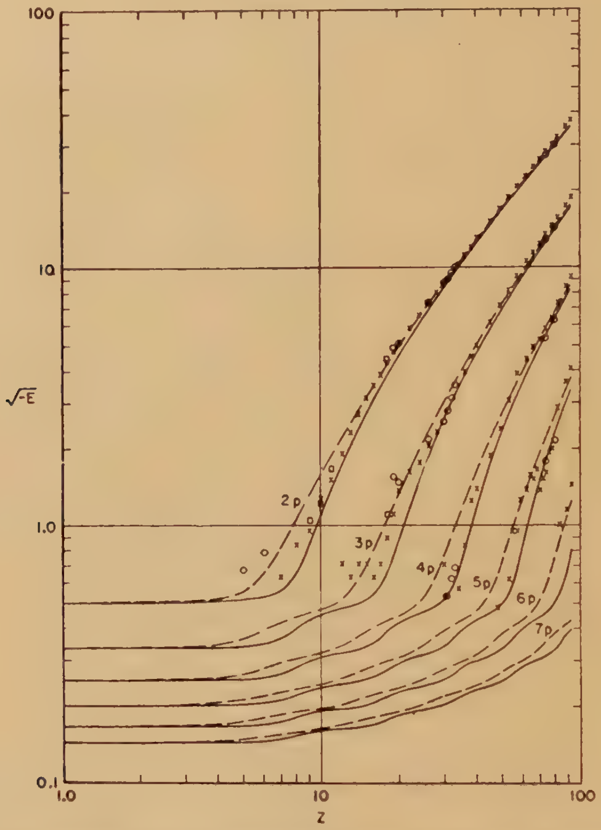
Fig. 8



Comparison of square root of computed s-levels with experimental values. Energies are in Rydbergs.
Solid line—results using modified TF potential (5.20).
Dashed line—results using modified TFD potential (5.23).
Circles—results using Hartree method.
Squares—results using Hartree–Fock method.
Crosses—experimental values.
(From Latter 1955 a.)

of fig. 1. The form given by Latter (1955 a) and quoted in eqn. (5.22) is much the most accurate of these, but from a practical point of view will be unmanageable except by entirely numerical methods, in which case it is usually better to work directly from the exact numerical values. (The most convenient tabulation of the isolated atom solution is that of Kobayashi *et al.* (1955), where the derivative ϕ' is also given.) We shall not go into all the proposed forms, but will make reference to an investigation by Umeda (1954 ; see also Umeda and Kobayashi 1955) of the merits of the various types of approximate analytic solutions, where most of the references are given.

Fig. 9



Comparison of square root of computed p-levels with experimental values. Energies are in Rydbergs.
Solid line—results using modified TF potential (5.20).
Dashed line—results using modified TFD potential (5.23).
Circles—results using Hartree method.
Squares—results using Hartree–Fock method.
Crosses—experimental values.
(From Latter 1955 a.)

However, we shall briefly discuss one of the most interesting of the methods used to find an approximate solution for atoms, due to Brinkman (1954), as it appears capable of fairly direct extension to obtain results for molecules (see § 6). Brinkman writes eqn. (4.2) in the form

$$\frac{d^2\phi}{dx^2}=(x\phi)^{1/2}\frac{\phi}{x}$$

and notes that for 'intermediate' values of x, $(x\phi)^{1/2}$ is a slowly varying function. Treating this as a constant, a solution of the resulting linear equation may be written

$$\phi = Cx^{1/2}K_1(2\{x\phi\}^{1/4}x^{1/2}) \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.24)$$

where C is an arbitrary constant, while K_1 is a modified Bessel function of the second kind. Brinkman takes the values of the 'constants' as $C = 1{\cdot}73$ and $\{x\phi\}^{1/4} = 0{\cdot}8$, apparently by fitting (5.24) to the exact solution. The results thus obtained from (5.24) are correct to within a few per cent in regions where ϕ is of a significant size, but the solution has the wrong asymptotic form for large x.

In conclusion, it seems fair to say that such analytical approximations are of very limited value now that the exact numerical solution is available.

§ 6. MOLECULES

We pass on now to discuss the application of the TF approximation to molecular problems. In this field, except in the case of a few simple molecules, much less information has as yet been forthcoming by accurate application of the ideas of the Hartree self-consistent field method, although the formulation of the approximate self-consistent field scheme based on the linear combination of atomic orbitals approximation (Roothaan 1951) has begun what appears to be a new era in molecular work ; and at last wave functions of significant quantitative accuracy are beginning to appear. Nevertheless, at this early stage in the development of self-consistent field methods for molecules, it seems likely that the TF approximation can be particularly valuable in molecular theory. Of course, even the use of this simplified approximation involves very considerable mathematical difficulties, chiefly due to the non-linearity of the basic equation. However, in the last four or five years some very definite progress has been made, and we shall consider the most important work in some detail.

6.1. *Diatomic Molecules*

6.1.1. *Homonuclear molecules.*

In the case of homonuclear diatomic molecules, no solution of the TF equation has yet been obtained which supersedes the important early work of Hund (1932) for N_2 and F_2 (for a discussion of Hund's method, see also Gombás 1949), and so we shall not go into these applications in much detail. However, the TFD equation has been solved for various internuclear distances for N_2 by Sheldon (1955) and we shall discuss this work later, although it is based on Jensen's interpretation of the isolated atom and is therefore open to possible objections on these grounds.

(i) *Analytical attempts to solve the TF equation.* Dealing first with the unmodified TF equation, Lopuszanski (1950) has attempted an analytical attack which we shall refer to very briefly. The basic idea is to obtain approximate solutions in two extreme cases, firstly in the immediate neighbourhood of the nuclei and secondly at large distances from the nuclei. It is then proposed that the gap between the solutions be bridged by polynomial interpolation. In essence, the method is rather similar to that of Hund, who also introduced an interpolation function to allow the joining up of two solutions of correct limiting form. Hund's method however has the considerable advantage that the TF solution for atoms is used as the basic function from which the solution for molecules is constructed, whereas Lopuszanski starts from the less accurate approximation of Sommerfeld (1932). No application of Lopuszanski's method is, however, available.

Another attempt to solve the TF equation analytically has been reported by Brinkman (1954) whose work on atoms has already been referred to briefly in § 5.6. Brinkman follows Hund in seeking an approximate solution of the form

$$V \doteq \frac{Ze}{b}\left[\frac{F(x_1)}{x_1}+\frac{F(x_2)}{x_2}\right] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6.1)$$

where $x_1=r_1/b$, $x_2=r_2/b$; r_1 and r_2 being the distances from the two nuclei in the molecule. Of course it is not possible to get an exact solution of this form, but Hund's work suggests that this should be a fairly good approximation. If we substitute (6.1) in the TF equation for the potential then we have

$$\frac{1}{x_1}\frac{d^2F(x_1)}{dx_1{}^2}+\frac{1}{x_2}\frac{d^2F(x_2)}{dx_2{}^2} \doteq \left[\frac{F(x_1)}{x_1}+\frac{F(x_2)}{x_2}\right]^{3/2}.$$

In order to obtain approximate solutions of this equation, Brinkman now looked for an approximately constant factor in the right hand side. Defining a quantity

$$A=\frac{F(x_1)}{x_1}+\frac{F(x_2)}{x_2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6.2)$$

Brinkman found that x_1A was reasonably constant near the first nucleus, and x_2A near the second. He thus separated the equation to obtain the approximate result

$$d^2F/dx^2=(xA)^{1/2}F(x)/x^{1/2} \quad . \quad . \quad . \quad . \quad . \quad (6.3)$$

with solution

$$F(x)=Cx^{1/2}K_{2/3}(\tfrac{4}{3}\{xA\}^{1/4}x^{3/4}). \quad . \quad . \quad . \quad . \quad . \quad (6.4)$$

The expression (6.4) was then substituted into (6.1) putting $(xA)^{1/4}=0{\cdot}82$ (estimated by substituting the atomic potential functions for F) and the constant C was chosen in such a way that the potential approximates to the potential of atomic nitrogen near the nuclei. In this way, results were obtained which were graphically indistinguishable from those of Hund. It may therefore be that this method will be useful when applied to other diatomic molecules, but no new results have as yet been obtained. However, an extension of this technique has been applied by Brinkman and Peperzak (1955) to the water molecule (see § 6.3.1).

(ii) *Effect of molecular binding on inner-shell electrons.* Another interesting investigation concerning diatomic molecules has been made by Reiss and Saltsburg (1950). These writers have attempted to assess the disturbances in the inner shells of such molecules due to molecular binding, and their basic method can be described qualitatively as follows. Near a nucleus of the diatomic molecule, the charge distribution will be spherically symmetrical, and the same as that in an isolated atom. At some point further from the nucleus, along the bond axis say, some asymmetry will begin to manifest itself, and it is then no longer possible to regard the distribution as spherical. The fraction of electrons beyond this point might be regarded as disturbed by molecular binding. The main part of the paper is devoted to the establishment of a criterion by means of which the 'asymmetric point' can be found, and the results are then used to estimate the number of electrons disturbed by binding in homonuclear diatomic molecules of the halogen and alkali groups. For the detailed argument used to obtain the necessary criterion referred to above, the original paper must be consulted. However, the results obtained are of some interest and will be summarized here. Table 2 shows the average number of electrons disturbed, N, as defined by Reiss and Saltsburg. It can be seen that according to this work, the disturbance due to molecular binding for Na_2, K_2, Cl_2, Br_2, and I_2 penetrates only as far as the shell directly below the valence shell, whereas in the case of Cs_2 the disturbance penetrates somewhat beyond the first subshell.

Table 2. Average Number of Electrons per Atom Disturbed by Molecular Binding

Element	Na	Cl	K	Br	I	Cs
Atomic number	11	17	19	35	53	55
N	5·7	11·0	8·5	17·5	24·1	22·2

A plot of N against atomic number leads to the dotted curve shown in fig. 10, and it will be noticed that the disturbances are less for the alkalis than for the halogens. (The periodic behaviour found should occasion no surprise as arising from a statistical model, for the experimental internuclear distances have of course been put into the theory, and the halogen distances are much less than the alkali values.) It will be seen from fig. 10 that for both the alkalis and the halogens the plots of N against Z are almost straight lines and can be represented by the approximate formulae

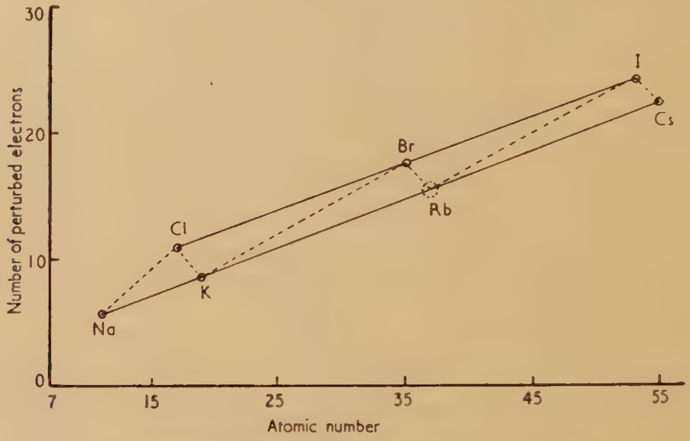
$$N = 4{\cdot}73 + 0{\cdot}366Z \quad \text{(Halogens)}$$

$$N = 1{\cdot}47 + 0{\cdot}377Z \quad \text{(Alkalis).}$$

Reiss and Saltsburg used the second of these formulae to predict the internuclear distance for Rb_2, for which no data is available at present.

The result they obtain is 4·28 Å. to be compared with the distance between nearest neighbours in the metal of 4·32 Å. The value 4·28 Å at least agrees with the experimental fact that the internuclear distances in the other alkali diatomic molecules are all slightly less than the values for the metals.

Fig. 10



Average number of electrons disturbed by molecular binding for alkalis and halogens.
(After Reiss and Saltsburg 1950.)

(iii) *The nitrogen molecule, with exchange included.* By far the most complete investigation carried out on a diatomic molecule is that of Sheldon (1955) for N_2. As we have already mentioned, Hund (1932) obtained an approximate solution of the TF equation for the ground state of this molecule. The work of Sheldon is based on the TFD equation, and is essentially a generalization to a molecule of the arguments given earlier by Jensen (1935) for an atom. We believe this work on N_2 is open therefore to possible objections of the kind discussed in § 4 ; in particular the fact that the molecule in this scheme has a discontinuity in the charge density at the boundary is unsatisfactory.

Nevertheless, there is no doubt whatever that the results of this work, particularly the fields obtained, have a good deal of significance, for only in the outer regions of the molecule will they be at all seriously affected by the detailed conditions imposed at the boundary. For representations of the statistical fields for the first four internuclear distances shown in table 3, reference should be made to figs. 2, 3, 4 and 5 of Sheldon's paper. A detailed discussion of the elaborate numerical technique used to deal with this problem will also be found there.

In addition to these fields, which should be of direct value for certain kinds of physical applications (e.g. see Recknagel 1934 and Bullard and Massey 1933) as well as providing a good starting point for more accurate self-consistent field calculations, Sheldon also made calculations of the total energy of the molecule as a function of the internuclear distance, to see whether his treatment would predict a stable molecule. For the details the original paper must be consulted, but the final numerical results are of considerable interest and we give them in table 3 (prepared from Sheldon's table). The second row of table 3 shows the number of electrons corresponding to the numerical solutions obtained by Sheldon; the exact solutions would of course lead to 14 electrons in each case. In the following rows the various contributions to the energy are listed, and the total energy obtained by summing these is shown. It will be noted that according to the values thus obtained there is a minimum in the total energy, and therefore a stable molecule is predicted. However, Sheldon believes this result to be incorrect, and to arise from errors in the potential energy terms as given. Certainly, the total potential energy, not given in Sheldon's table but recorded in table 3 for convenience, seems to indicate quite significant errors when the variation with internuclear distance is examined. The change in energy ΔE relative to the energy for an internuclear distance of 16·0 atomic units as obtained from the total energies recorded in table 3 is also shown for comparison with $\Delta E'$, the change in energy referred to the same level but obtained by numerical integration of a force. It will be seen that $\Delta E'$ predicts no stable molecule, and from an examination of the errors involved in the two quantities ΔE and $\Delta E'$ Sheldon concludes that $\Delta E'$ is the more accurate value. In fact he draws the general conclusion that the statistical treatment, in the form used by him, will not lead to binding for any molecule.

Table 3. Summary of Sheldon's Energy Calculations for N_2
(atomic units are used)

Internuclear separation	1·0	2·076	3·0	6·0	16·0
Number of electrons	13·99	13·89	13·95	13·95	13·95
Kinetic energy	166·73	157·14	156·83	156·04	155·82
Electron–nuclear potential energy	−444·68	−400·02	−387·93	−371·35	−360·93
Electron–electron potential energy	92·20	77·20	71·33	63·62	58·58
Nuclear–nuclear potential energy	49·00	23·60	16·33	8·17	3·06
Total potential energy	−303·48	−299·22	−300·27	−299·56	−299·29
Exchange energy	−13·70	−12·72	−12·60	−12·47	−12·45
Total energy	−150·39	−154·80	−156·04	−155·99	−155·92
ΔE	5·53	1·12	−0·12	−0·08	0
$\Delta E'$	6·06	1·08	0·62	0·03	0

Finally, in connection with the N_2 molecule, the calculation of the magnetic susceptibility by Bonet and Bushkovitch (1953) should be mentioned. This work, carried out before the results of Sheldon were available, included exchange and correlation in an approximate way, the electron distribution obtained earlier by Hund (1932) in the unmodified TF approximation being adjusted to give the required boundary density on a prolate spheroidal surface. In other words, the density breaks off abruptly at such a surface, just as in Jensen's model of the isolated atom and in Sheldon's work. The final result for the molar magnetic susceptibility obtained by Bonet and Bushkovitch was -25×10^{-6}, to be compared with a mean observed value of -13×10^{-6} and the agreement is satisfactory in view of the numerous approximations involved.

6.1.2. *Heteronuclear molecules*

Glazer and Reiss (1953), in an interesting paper, discussed the solution of the TF equation for iodine chloride by the relaxation method of Southwell. We do not propose to discuss the details of the relaxation technique employed by these authors here, although it is of obvious importance should additional work for other cases be thought desirable. Electron density contours were given for ICl, and from this charge distribution the dipole moment was evaluated. The result given by Glazer and Reiss is 0·3 Debye units in the correct sense and in reasonable agreement with the experimental value of 0·57 Debye units. However, later work seems to cast some doubt on the validity of this result (see § 6.5).

Nevertheless, the method of solution developed by Glazer and Reiss seems certainly the most promising approach for such molecules and results for the charge distribution and potential field such as these workers obtained for ICl would seem to afford an extremely useful starting point for more accurate work.

6.2. *Molecules with High Symmetry*

From the consideration of diatomic molecules, we turn now to molecules with tetrahedral and octahedral symmetry. In one sense these are simpler to handle in a plausible approximate manner than the diatomic molecules, for as emphasized by Buckingham *et al.* (1941) it seems reasonable in a molecule such as CH_4 to average the nuclear field over angles, and to consider the motion of the electrons in the resulting central field. For CH_4, Buckingham *et al.* after making this 'smoothing approximation', carried through a Hartree self-consistent field calculation with gratifying results. In view of the success of this calculation, it seemed worthwhile to develop a somewhat general treatment of such highly symmetrical molecules by means of the TF theory (March 1952 c).

6.2.1. *Formulation of the problem*

We shall deal quite generally, in formulating the basic scheme, with the molecules XY_n, where $n=4$ or 6, and we suppose that the nuclei of the Y atoms are smeared out uniformly over the surface of a sphere of radius R with the X atom at the centre. Let Ze be the positive charge of the central atom, and let N be the total number of remaining positive charges. The surface density σ is then given by

$$\sigma = Ne/4\pi R^2. \qquad \text{(6.5)}$$

We must consider the two regions $r < R$ and $r > R$ separately. Let the electrostatic potentials in the two regions be V_1 and V_2 respectively. Then the boundary conditions may be written

$$\left.\begin{array}{lll} (a)\ V_1 \to Ze/r & \text{as} & r \to 0 \\ (b)\ V_2 \to 0 & \text{as} & r \to \infty \\ (c)\ (V_1)_R = (V_2)_R & & \\ (d)\ -\left(\dfrac{dV_1}{dr}\right)_R + \left(\dfrac{dV_2}{dr}\right)_R = -4\pi\sigma & & \end{array}\right\} \qquad \text{(6.6)}$$

The condition (d) follows immediately from a well known result in electrostatics for the discontinuity in the field across a surface distribution of charge. In terms of the usual TF function $\phi(x)$ defined by

$$V = \frac{Ze}{r}\phi, \qquad r = bx,$$

these conditions become

$$\left.\begin{array}{lll} (a)\ \phi_1(0) = 1 & & \\ (b)\ \phi_2 \to 0 & \text{as} & x \to \infty \\ (c)\ \phi_1(X) = \phi_2(X) & & \\ (d)\ \left(\dfrac{d\phi_1}{dx}\right)_X - \left(\dfrac{d\phi_2}{dx}\right)_X = \dfrac{N}{XZ} & & \end{array}\right\} \qquad \text{(6.7)}$$

X here is the radius of the sphere of surface charge in dimensionless units.

Going back to fig. 1, we can see immediately that the solution represented by (iii) out to X, and afterwards by (iv), represents an acceptable solution satisfying the above boundary conditions, and the particular molecule which such a solution describes is determined by the difference in the slopes of the curves at X, as we see from the condition (d) above.

It is a fortunate circumstance that all solutions which tend to zero at infinity can be expressed in terms of two master solutions, as was discussed by the writer (March 1952 c). These were tabulated once and for all, together with ten solutions of the dimensionless TF equation for use in the inner region $x < X$.† Thus, a quite general scheme is provided, by means of which charge distributions and potential fields can be obtained for molecules to which the ‘ smoothing approximation ’ is applicable.

6.2.2. *Energetic considerations*

It is of obvious interest to calculate the energy of the molecules as a function of the X–Y distance, for in principle the bond lengths and force constants of the molecules may thereby be predicted. The total energy is given by eqn. (2.6), provided that we put in the appropriate values of V_N and U_N. We have for V_N, the potential due to a nuclear framework consisting of a point charge Ze at the origin and a spherical surface distribution of density $Ne/4\pi R^2$,

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† Many additional solutions which can be used in this region are now available (Latter 1956).

$$\left.\begin{aligned} V_{N1}&=\frac{Ze}{r}+\frac{Ne}{R} \\ V_{N2}&=\frac{Ze}{r}+\frac{Ne}{r} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6.8)$$

For the evaluation of U_N, we use the distribution of nuclei which actually occurs in the molecule and not our hypothetical distribution. (The basic justification of this resides in the variational status of the method, as discussed by Ballinger and March (1955 c). They show that the densities obtained from the scheme developed in § 6.2.1 are the best possible spherical densities in the sense of the variation method.) It can then be shown very easily that

$$U_N=\frac{Ne^2}{R}[Z+cN] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6.9)$$

where

$$c=\frac{3\sqrt{6}}{32} \quad \text{for tetrahedral molecules}$$

$$=\frac{1+4\sqrt{2}}{24} \quad \text{for octahedral molecules.}$$

Furthermore, and most important from a practical point of view, explicit formulae can be obtained for the energy, and for the derivative of the energy with respect to the internuclear distance, thus avoiding further quadrature, just as Milne showed was possible for isolated atoms. The expressions for E and $d\mathrm{E}/dR$ can be written

$$\mathrm{E}=\frac{3}{7}\frac{Z^2e^2}{b}\left[a_2+\frac{4}{3}\frac{N}{Z}\frac{\phi_1(X)}{X}-\frac{1}{3}\frac{N}{Z}\left(\frac{d\phi_1}{dx}\right)_X-\frac{N^2}{XZ^2}+\frac{7c}{3}\frac{N^2}{XZ^2}\right] \qquad (6.10)$$

where a_2 is the slope of ϕ_1 at the origin ;

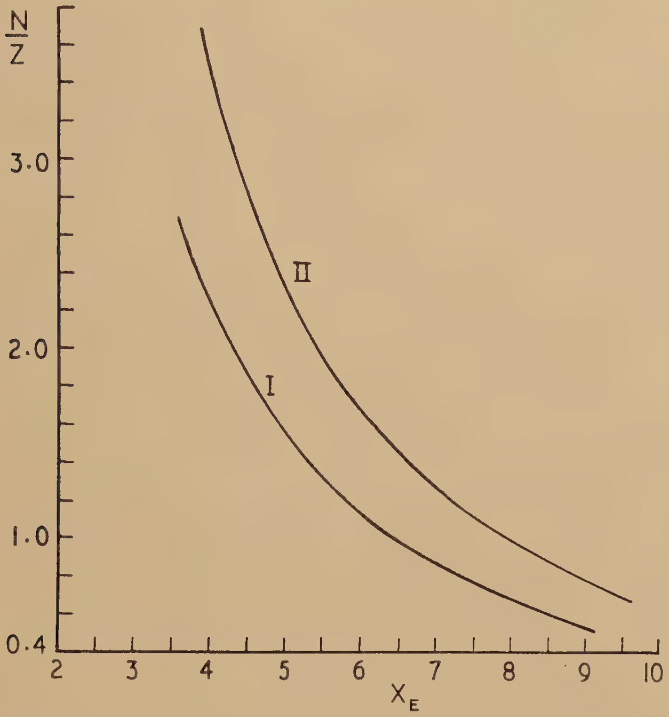
$$\frac{d\mathrm{E}}{dR}=\frac{ZNe^2}{R^2}\left[X\left(\frac{d\phi_1}{dx}\right)_X-\phi_1(X)-c\frac{N}{Z}\right]. \quad . \quad . \quad . \quad . \qquad (6.11)$$

Originally the eqn. (6.11) for $d\mathrm{E}/dR$ was obtained by a rather lengthy method, starting again from the initial energy expression and differentiating it immediately with respect to R. It can however, be written down very simply by noting that it is directly related to the electric field at the surface distribution due to the electrons. Further, the virial theorem is satisfied in the form

$$2T+U=-R\frac{d\mathrm{E}}{dR}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6.12)$$

The eqn. for dE/dR demonstrates immediately the possibility of a minimum in the energy curves as a function of the $X-Y$ distance, and the results may be represented in a very simple and general form by plotting N/Z against the equilibrium internuclear distance in dimensionless units X_E. The results are shown in fig. 11, curve I referring to tetrahedral, and curve II to octahedral molecules. Curve I has been represented by Bowers (1953) by the approximate analytic form

Fig. 11



N/Z against equilibrium sphere radius in dimensionless units.
Curve I, tetrahedral molecules.
Curve II, octahedral molecules.
(After March 1952 c.)

$$R_E = Z^{-1/3}\, 3{\cdot}12 \left(\frac{N}{Z}\right)^{-0{\cdot}6} \text{Å}, \quad . \quad . \quad . \quad . \quad . \quad (6.13)$$

the range of validity being given by $0{\cdot}8 < N/Z < 3{\cdot}0$. Bowers also calculated the second derivative of the energy with respect to the internuclear distance at the minimum of the energy curve, and this can be represented by the approximate expression

$$\left(\frac{d^2E}{dR^2}\right)_{R_E} = 1980 Z^3 \left(\frac{N}{Z}\right)^{3{\cdot}51} \text{dynes/cm}, \quad 0{\cdot}8 < \frac{N}{Z} < 3{\cdot}0. \qquad (6.14)$$

This leads to force constants and we shall discuss it later.

However, a comparison between theoretical and experimental bond lengths makes it clear that there is little agreement. For example, as can easily be shown from fig. 11, for CH_4 the experimental bond length is about a half of the theoretical value while for SiF_4 and SF_6 it is about twice as large as the theory gives. The only conclusion that can be drawn therefore is that in this approximation the method is inadequate for energetic considerations. The most probable causes of the poor results thus obtained appear to be the 'smoothing approximation' employed, and the neglect of exchange. However, at least for CH_4 it seems from the work of Buckingham *et al.* that the 'smoothing approximation' is not leading to very serious errors and thus it appeared likely that the introduction of exchange would improve the results very considerably. This is, in fact, the case, as we shall show in the following paragraph.

6.2.3. *Introduction of exchange for methane, silane and germane*

Some of the generality of the previous treatment is lost when exchange is introduced, and so far detailed calculations have been made only for CH_4, SiH_4 and GeH_4 (Ballinger and March 1955 b). The method used was an extension of that introduced by Scott for atoms, and thus the difficulties associated with the TFD equation are again circumvented. The unmodified TF densities, calculated in the manner we have described, were used as variation functions for calculating the energy including exchange. The values thus obtained for the bond lengths and force constants for the totally symmetric vibrations (simply $(d^2E/dR^2)_{R_E}$) are shown in table 4, together with the experimental results. Also, for purposes of comparison, we show the TF results neglecting exchange for the bond lengths of CH_4 and SiH_4, and an approximate value for the force constant of CH_4 which was obtained by using formula (6.14) slightly

Table 4. Bond lengths in Å

	Experimental	TF	TF with exchange
CH_4	1·09	2·1	1·38
SiH_4	1·46	2·5	1·62
GeH_4	1·48	—	1·9

Force constants in units of 10^5 dynes/cm

	Experimental	TF	TF with exchange
CH_4	20	1	9
SiH_4	11	—	5
GeH_4	10	—	3

outside its proper range of validity. It can be seen that the results for the three molecules are in quite reasonable agreement with experiment, especially in view of the complexity of the whole problem and the approximations which have been made. From a general point of view, two further observations can be made. First of all, the experimental trends both for bond lengths and force constants, clearly emerge from the calculations. Secondly, it is not surprising that the force constants are smaller than the experimental values, since the calculated bond lengths are too large. The fact that we obtain weaker and longer bonds by the TF method than actually exist is in general agreement with a conclusion reached earlier by the writer (March 1952 a ; see also § 6.4) from a theoretical discussion of the electron distribution in benzene, that the TF theory in this case exaggerates the presence of the atoms at the expense of the bond character.

Apart from these general remarks however, the detailed results for the molecular constants are rather interesting. For example, as we go from CH_4 to SiH_4, the error in the bond length decreases from 27% to 11% which is very satisfactory. The force constant for SiH_4 is in error by about the same amount as the CH_4 force constant. But for GeH_4 the bond length is in error by about 25%, which seems surprising at first sight in view of the fact that the TF method would be expected to become more accurate for heavier molecules. Some explanation of this is to be found in an observation made by Heath *et al.* (1950), from consideration of regularities in bond lengths and force constants for a whole series of molecules, that the bond in GeH_4 is probably ‘ abnormally strong and short ’. If this is the case, it is not to be expected that the TF approximation, which distinguishes different atoms simply by a change of scale depending on the atomic number, could give any explanation of such behaviour.

Finally, it is quite practicable, if somewhat laborious, to obtain the energy for a particular molecule as a function of the internuclear distance and to examine how this energy curve is built up from its separate components. The results of such a calculation for SiH_4† are shown in fig. 12, for a limited region around the equilibrium bond length. These results were actually found using a somewhat improved variation function analogous to that discussed in § 5.2 for atoms. The effect of the scale factor on the separate energy curves is marked, but the total energy is left virtually unchanged. Whilst these energy curves cannot be quantitatively accurate unless a ‘ boundary correction ’ is applied, the main characteristics of the correct energy curves for SiH_4 should be shown by fig. 12. This is because the ‘ boundary correction ’ will arise mainly from the silicon K-shell electrons (see § 5.1), and therefore ought to be practically independent of R in the important region around the equilibrium position. The energy curves obtained by the method outlined here seem to be the first to be given explicitly for a polyatomic molecule.

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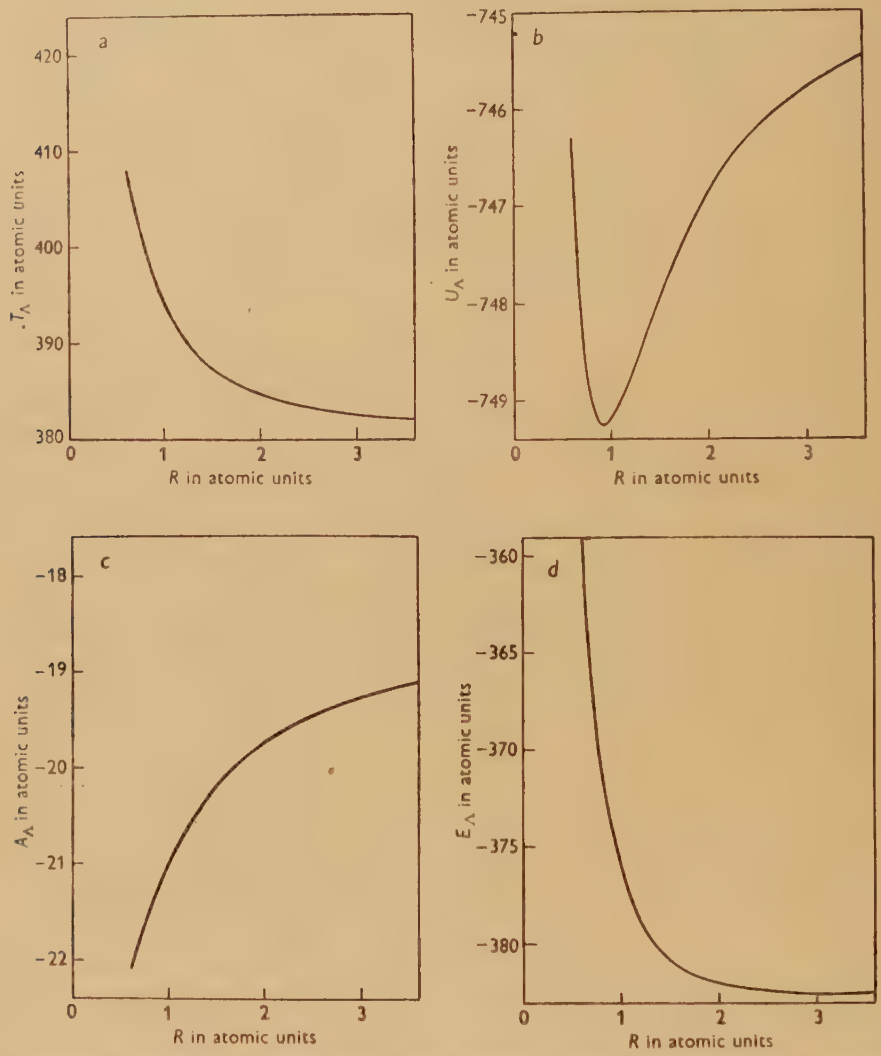
† Carter (1956) has very recently calculated a Hartree field for SiH_4, using the ‘ smoothing approximation ’.

Fig. 12



Variation with Si–H distance of (*a*) kinetic energy, (*b*) potential energy, (*c*) exchange energy, (*d*) total energy.
(From Ballinger and March 1955 b.)

6.2.4. *An improved electron distribution in methane*

So far, in this discussion of molecules with high symmetry, we have dealt only with the simplified case when we make the 'smoothing approximation'. Recently however, Glazer and Reiss (1955) have made a notable advance in the theory by attempting a more direct numerical solution of the TF equation for CH_4. In their work, planes are drawn which divide the molecule into four pyramids, each enclosing a C–H bond. The problem of solving the TF equation in one of these pyramids, subject to the boundary conditions required by the symmetry of molecule, is too difficult at present, and Glazer and Reiss made the approximation of replacing the pyramid under consideration by a cone of equal volume. Having done this, the TF equation was then solved for the potential on a high-speed computer, and in this way an electron density map was constructed for CH_4.

The primary concern of Glazer and Reiss, however, was to calculate the dipole moment of the C–H bond in the molecule. This quantity, whilst not susceptible to direct measurement, is of considerable interest, and has been a source of controversy for a number of years (see, for example, Gent 1948 and Smith 1953). In order to obtain a value for the dipole moment using the present model it was necessary to solve the TF equation for carbon alone as well as for carbon and hydrogen, within the equal volume cone. The dipole moment may then be obtained by taking the difference between results calculated from these two solutions, and the value thus found by Glazer and Reiss was 2·8 Debye units $C+H-$. This value is almost certainly much too large, but the polarity agrees with that found by Coulson (1942) and Mueller and Eyring (1951), who suggest moments of 0·4 and 0·2 Debye units respectively.

Whilst the TF method does not seem well suited for dipole moment calculations, the results of which appear to depend sensitively on the details of the charge distribution (see also § 6.5), the solution of the TF equation obtained by Glazer and Reiss for CH_4 is the most accurate yet found for any polyatomic molecule †. It would at present however be out of the question to make energy calculations with such a complex electronic distribution.

6.2.5. *Molecules with heavy atoms in the outer positions*

It seems clear from the previous considerations that for CH_4, SiH_4 and GeH_4 the 'smoothing approximation' is very useful. Unfortunately the same does not appear to be true for molecules whose outer atoms have groups of highly localized inner-shell electrons. This was first pointed out by the writer from an examination of the charge distribution in CCl_4 (March 1952 c). Here it is found that the use of the naive 'smoothing approximation' causes far too many inner-shell electrons to move away from the region around the chlorine nuclei. An alternative approximation in which the inner-shell electrons of chlorine were compressed into the nucleus and the remaining charges smoothed, appeared in some ways to lead to more reasonable results, although basically the treatment is unsatisfactory as the exclusion principle is ignored. Confirmation of these findings is provided by the work of Bowers (1953), who examined the relation between theory and experiment for a series of tetrachlorides and tetrabromides. He found that the results using the 'smoothing approximation' in its straightforward form were in disagreement with the experimental data, the force constants for the totally symmetric vibrations being completely the wrong order of magnitude.

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† *Note added in proof.*—The writer has recently been informed that a numerical slip has occurred in the course of this calculation and the results should therefore be treated with some reserve.

Thus it is clear that, at least in the present form, the most that can be expected for such molecules is that the method will provide a semi-empirical scheme which will allow some correlation of the experimental data to be made, and this was the line taken by Bowers. The results, based on the formulae (6.13) and (6.14) which as Bowers pointed out were sometimes extrapolated in unwarranted fashion, can be summarized as follows :

(i) For the series of chlorides and bromides, the Z dependence of R_E predicted by the theory (without exchange of course) is $Z^{0\cdot27}$ whereas the observed dependence is $Z^{0\cdot12}$.

(ii) The Z dependence of the force constant k, (defined simply as $(d^2E/dR^2)_{R_E}$) given by the theory is a decrease as $Z^{-0\cdot51}$, whereas experimentally the data show a decrease which cannot however be represented by a constant exponent over the whole range of Z. For the heavier chlorides (Ge, Sn, Pb) the exponent is about $-0\cdot45$.

(iii) Using the idea of an effective nuclear charge as suggested by the writer's results on the charge distribution in CCl_4, Bowers used the experimental bond lengths to calculate an effective charge, N_{eff} say, from (6.13) and then used formula (6.14) to calculate the force constants for the totally symmetric vibrations. The results for the tetrachlorides are shown in table 5. It will be seen that there is now order of magnitude agreement, and there is a definite trend towards better results for the heavier molecules.

Table 5. Force Constants of Tetrachlorides in Units of 10^5 dynes/cm

	C	Si	Ge	Sn	Pb
N_{eff}	6·4	6·9	9·0	9·6	10·9
k (calculated)	5·4	4·5	7·4	7·5	8·9
k (experimental)	17·6	15·1	13·1	11·2	9·0

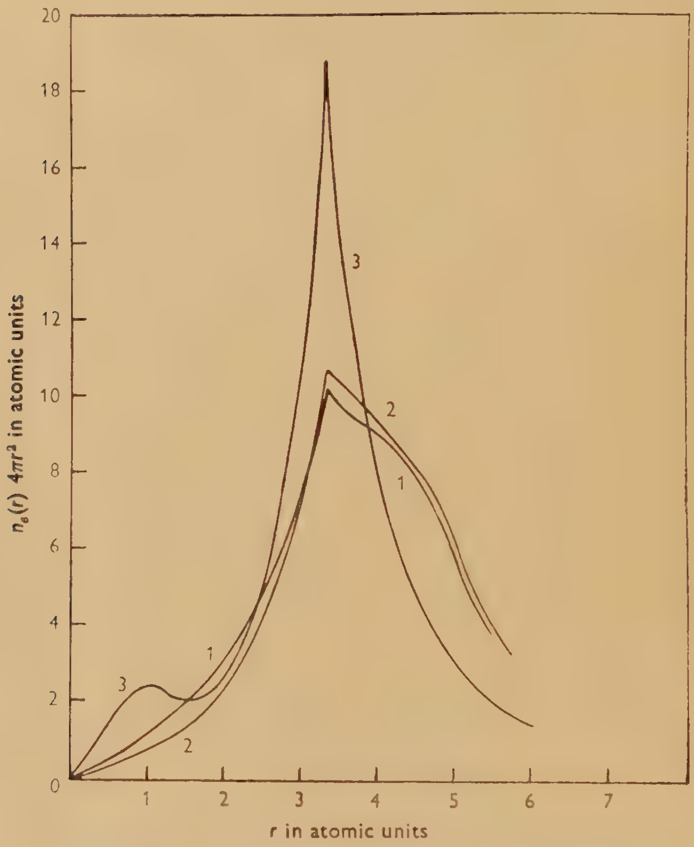
However, the effective nuclear charges shown in table 5 are considerably less than might be expected from an argument in which the inner-shell electrons are compressed into the nucleus. For tetrachlorides, N_{eff} might have been supposed naively to be about 28, although, as pointed out previously, the exclusion principle is ignored, and it seems plausible that by reducing N_{eff} somewhat the effect of the exclusion principle might be simulated.

Very recently, an attempt has been made to remove the difficulties associated with the neglect of the exclusion principle in the method of effective nuclear charges, or, more correctly, in a generalization of it (Coulson and March 1956), and the results have been worked out in detail for CCl_4 (Banyard and March 1956 b). Although the scheme is essentially very approximate, it was hoped that it would perhaps give a useful overall account of the distribution of valence electrons in molecules with heavy outer atoms, which at present are very difficult to treat quantitatively by other methods. In this work the inner-shell electrons of the outer atoms are described wave-mechanically, assuming them to be undisturbed by molecular binding (this should be rather more accurate than the procedure of compressing the inner electrons into the nucleus from the point of view of the effective field in which the valence electrons move) and only the valence electrons are treated by the TF method. An effective potential in which the valence electrons are assumed to move is then obtained by averaging the distribution of inner-shell electrons over all angular orientations and also averaging the nuclear framework exactly as before. The inner-shell electrons of the central atom are also replaced by an effective potential, which is consistent with the general approach of separating inner-shell and valence electrons. Thus, adding these potentials together with the self-consistent field due to the valence electrons, an effective potential in which the valence electrons move is known. Of course, we do not know the self-consistent field due to the valence electrons until the problem has actually been solved.

However, the TF method cannot be used directly to describe the valence electrons, since the inner-shell electrons have been replaced by an effective field, and there is nothing as yet to prevent the valence electrons falling into the lower levels associated with this field. In fact we ought to begin filling up the energy levels with the valence electrons only when sufficient levels are left vacant to account for the inner-shell electrons. The level at which the valence electrons begin to be accommodated can be found within the statistical framework in the following way. Assuming for the moment that the total electrostatic potential in the molecule is known, the statistical theory can be used in a straightforward manner to calculate the number of levels in any given energy range dE. Knowing this, we can easily find the energy below which the inner-shell electrons can just be accommodated, and hence the level at which the valence electrons enter is known. The TF method may then be applied in a straightforward manner to describe the valence electrons, and the scheme is continued by an iterative process until it is self-consistent; that is until the level at which the valence electrons begin to fill up reproduces itself.

For further details of the scheme we refer the reader to the original papers, but it is of interest to consider briefly the results obtained for CCl_4. If $n_v(r)$ is the number of valence electrons per unit volume, the radial charge distribution of valence electrons, defined as $n_v(r)4\pi r^2$, is shown in fig. 13. Curve 1 has been obtained by the scheme outlined above, curve 2 is the result of a naive application of the 'smoothing approximation' as described in § 6.2.1, the valence electron distribution being then extracted from the total density thus obtained, while curve 3 is the result obtained by compressing the inner-shells into the nuclei and neglecting the exclusion principle.

Fig. 13



Radial charge distribution of valence electrons in CCl_4.
(From Banyard and March 1956 b.)

It will be seen that there is quite good agreement between curves 1 and 2, and curve 3, involving the neglect of the exclusion principle, will certainly be the least accurate. The similarity between curves 1 and 2 can only mean that the details of the distribution of inner-shell electrons are relatively unimportant. This is because curve 2 was calculated by a naive application of the 'smoothing approximation', which certainly leads to an incorrect inner-shell density. Nevertheless, these inner-shell electrons are playing an essential role by allowing the exclusion principle to operate. Various considerations tend to indicate that curves 1 and 2 are giving too diffuse a charge cloud however, and the correct result would seem to lie between curves 1 and 3, although considerably nearer to curve 1. Whether a method such as that outlined here can lead to results of quantitative accuracy for molecules with heavy outer atoms seems, at present, to be open to question, but the results obtained for CCl_4 should at any rate form a useful starting point for more accurate work.

6.3. *Electron Distribution in Water and Phosphine*

6.3.1. *The water molecule*

Brinkman and Peperzak (1955) have applied the procedure of approximate linearization of the TF equation to the problem of obtaining an approximate solution for H_2O. Following Hund (1932) the electrostatic potential is written approximately as the sum of three terms;

$$V \doteqdot V_O(r_1) + V_H(r_2) + V_H(r_3)$$

where r_1 is the distance from the O atom, r_2 and r_3 are distances from the two H atoms. An approximate solution for V_0 may be obtained in terms of modified Bessel functions of the second kind (cf. § 6.1.1), whereas V_H may be obtained in terms of exponential functions. Using the customary TF relation between density and potential an approximation can thus be obtained to the electronic distribution in the molecule, and charge contours have been plotted, both in the plane of the molecule and in planes parallel to this, at distances of approximately $\frac{1}{4}$ Å and $\frac{1}{2}$ Å. It should be pointed out that charge normalization is not ensured by the above procedure; nor, for that matter, by any method utilizing Hund's approximate method of solution. The treatment of PH_3 which will shortly be described circumvents this difficulty, and in principle would be applicable to H_2O. However this method, which depends on an expansion in spherical harmonics, will give a less good approximation to the solution of the TF equation than Brinkman's near the H nuclei. In any case, however, the results can hardly be expected to be quantitatively accurate in this region.

It is pertinent to remark here that the electron distribution in the water molecule seems now to be known to better accuracy than could be achieved by a TF calculation (Ellison and Shull 1953, 1955; Banyard and March 1956 a). What seems clear is that the distribution averaged over all orientations about the O nucleus will be given rather accurately by first averaging the nuclear field over angles; why this should be so is made more clear from the discussion of PH_3 given below. A distribution of electrons which should be a good approximation to the true distribution calculated from the TF equation can thus be obtained from the writer's work on nearly spherical molecules, discussed in § 6.2.1. A check on the technique of Brinkman and Peperzak would be afforded by calculating the s-term in the expansion of their electron density in spherical harmonics and comparing it with that obtained by the method of § 6.2.1; such a calculation would also provide a check of the charge normalization.

Until some such investigation has been made, it is very difficult to assess the accuracy of the method of Brinkman and Peperzak.

6.3.2. *The phosphine molecule*

As mentioned above, a quite different line of attack has been developed for PH_3 (Ballinger and March 1956), based on the treatment of nearly spherical molecules discussed in § 6.2.1 and as the basic method is rather generally useful we shall consider it in some detail. The natural extension of the ' smoothing approximation ' used in § 6.2.1 is to regard the electrons in the phosphine molecule as moving in the field of the phosphorus nucleus and of a circular line charge, corresponding to the smearing out of the three protons. The electron density for such a model of the molecule may evidently be expanded in Legendre polynomials and the first few terms are calculated in this work. Obviously to impose the boundary conditions rigorously at the line charge, an infinite number of Legendre polynomials must be included. Therefore the variation principle of the TF theory was taken as the basis of the calculation and the approximate variational density was written

$$n=n_0+\sum_{l=1,2,3} f_l P_l \quad . \; . \; . \; . \; . \; . \; . \; . \quad (6.15)$$

where n_0 and f_l are simply functions of the distance r from the phosphorus nucleus. Since over a large part of the molecule the phosphorus nucleus provides a predominant field of force, the explicit variational density was set up by substituting the approximate density in the TF equation (written in terms of the density)

$$\nabla^2 n^{2/3}=(4\pi e^2\mu^2)^{1/3} n \quad . \; . \; . \; . \; . \; . \; . \quad (6.16)$$

and treating the angular terms as small. The following approximate equations, which are taken as the defining equations for n_0 and f_l, then result ;

$$d^2\phi/dx^2=\phi^{3/2}/x^{1/2} \quad . \; . \; . \; . \; . \; . \; . \quad (6.17)$$

$$\frac{d^2\chi_l}{dx^2}=\chi_l\left[\frac{3}{2}\left(\frac{\phi}{x}\right)^{1/2}+\frac{l(l+1)}{x^2}\right], \qquad (l=1,\,2,\,3). \quad . \; . \; . \quad (6.18)$$

Here ϕ and χ_l are defined by

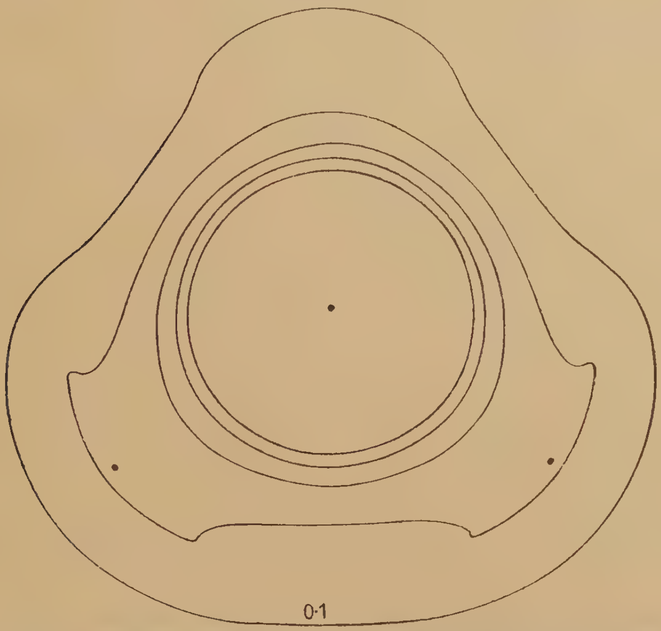
$$n_0=\frac{\mu}{4\pi e}\left(\frac{Ze}{r}\phi\right)^{3/2}, \quad . \; . \; . \; . \; . \; . \; . \quad (6.19)$$

$$f_l=\frac{3}{2}\frac{\mu}{4\pi e}\left(\frac{Ze}{r}\chi_l\right)^{3/2}, \quad . \; . \; . \; . \; . \; . \; . \quad (6.20)$$

and x is the usual dimensionless variable. It is then almost immediately evident that the spherical density n_0 is just that which has previously been discussed exhaustively for nearly spherical molecules. It is not surprising that this is so, for in obtaining the approximate equations we have assumed that the angular terms are small, and it can be shown that the density n_0 thus obtained is the best possible spherical density in the sense of the variational method (Ballinger and March 1955 c).

The functions f_l were now obtained by solving the eqns. (6.18) and when suitable behaviour at the origin and at infinity is required, these functions are each determined apart from a simple multiplier. These undetermined constants were then chosen by minimization of the total energy, in order to make this density as accurate as possible in the sense of the variational method. Detailed examination shows that the d-term (P_2 term) is small, and this was therefore neglected and attention focused on the p and f-terms, which were obtained explicitly. The energies obtained in the course of the application of the variational method are interesting. Using simply n_0 as the variational density leads to a total energy of $-426{\cdot}44$ atomic units, whereas the inclusion of f_1 and f_3 leads to a reduction in the energy of 0·35 atomic units. Such a small change makes it fairly clear that any modification of the first term n_0 in the variational density due to the inclusion of angular terms will be unimportant, and further calculations confirmed this completely. The conclusion is that a good approximation to the density averaged over angles is given by first averaging the nuclear field over angles. The results of the calculations are completely specified by giving ϕ, χ_1 and χ_3 (see fig. 2 of Ballinger and March 1956); but we display the density

Fig. 14



Electron density contours for PH_3 for a plane containing the molecular axis. Interval is 0·2 electron per cubic Å. Contours corresponding to densities greater than 0·9 electron per cubic Å are not shown. (From Ballinger and March 1956.)

for a plane containing the molecular axis in fig. 14 to show some of the main features of the results.

Briefly, it will be seen that the angular terms introduced in the treatment give at least some account of the P–H bonds, although the distribution near the H nuclei will not be an accurate representation of the proper TF density, as we have remarked previously. In fact, in the model under consideration there is a kind of distorted tubular distribution around the line charge, expressing the physical fact that there is some localization of electrons around the H nuclei. Furthermore, if we regard the molecule as being divided into two by a plane containing the P nucleus and parallel to the line charge, we can think of the additional charge which has been moved into the neighbourhood of the bonds by the introduction of angular terms as coming mainly from the other half of the molecule. It is interesting to note from fig. 14 that considerably more of this charge comes from around the continuations of the P–H bonds than from the molecular axis. In this latter region conventional molecular theories predict the presence of ‘ lone-pair ’ electrons, and it is felt that the density contours represent this to some extent.

It would seem reasonable to infer that for molecules such as H_2S and HCl a treatment along similar lines to that described for PH_3 should also be very useful. In fact, the densities in these cases, averaged over all orientations about the heavy atom, should be given to a good approximation by averaging the nuclear field spherically, and the resulting densities can then be easily obtained. An interesting test of the changes in the electronic distributions thus obtained through the series A, HCl, H_2S, PH_3 and SiH_4 might then be provided by experimental results on x-ray scattering, similar to those obtained by Thomer (1937) for scattering from Ne, H_2O, NH_3 and CH_4 in gaseous form. These latter results have been interpreted theoretically by Banyard and March (1956 a), and from their work it appears that the x-ray scattering is almost entirely determined by the s-term in the expansion of the density in spherical harmonics. Whilst in the case of this lighter series it is necessary to calculate explicitly wave functions for the molecules in order to obtain densities of significant accuracy, the heavier series should be such that the x-ray scattering properties can be reasonably well described by the statistical method.

Besides such direct applications, the field, including the angular terms, which has been obtained for PH_3 should provide an excellent starting point for the calculation of wave functions for this molecule, and further work along these lines is now being planned.

6.4. *The Benzene Molecule*

The only other attempt to solve the TF equation for a polyatomic molecule was made by the writer (March 1952 a) in a study of the distribution of electrons in the benzene molecule, an understanding of which is of central importance in organic chemistry. The study was carried out by using two distinct methods of finding the electron distribution, the TF method, and the more conventional molecular–orbital method in the linear combination of atomic orbitals approximation. Much of the interest in the work lies indeed in the comparison of the two sets of results, particularly as no experimental data are as yet available which can be compared directly with the calculated distributions. Since to discuss in detail the entire results of this investigation would take us too far from the main theme of this review, we shall confine ourselves to a brief description of the method used to solve the TF equation.

The six hydrogen atoms were first of all neglected, and an approximate solution of the TF equation was sought for a neutral system of six carbon nuclei arranged on a regular hexagon and thirty-six electrons. The hydrogen atoms were then finally superposed on the resulting electron distribution, an approximation which would not appear to be serious except in the centre of the C–H bonds. It will certainly hardly affect the charge distribution in the centre of the C–C bonds and at the centre of the benzene ring.

The solution of the problem when the hydrogen atoms are neglected was achieved by extending the method devised earlier by Hund (1932) for diatomic molecules, and to which brief reference has been made earlier. The essence of the treatment is to write down the appropriate solutions in the immediate neighbourhood of the nuclei and at large distances from them, and then to introduce an interpolation function to allow a smooth transition from one limiting solution to the other. In these calculations the interpolation function was taken to contain one adjustable parameter, which was chosen to make the approximate solution as accurate as possible.

The electron distribution thus obtained was plotted explicitly both in the plane of the benzene ring and in a parallel plane at a height of 0·35 Å above the plane of the ring. Similar density maps were also obtained by the molecular–orbital method and, considering the approximations inherent in both treatments, the overall agreement appeared satisfactory. As no experimental results were available for benzene, a tentative comparison was made with the density maps obtained experimentally for naphthalene and anthracene by Robertson and his co-workers[†]. There appeared to be reasonable overall agreement, but a naive comparison is not strictly fair as the effects of vibrations are very important, whereas, of course, the theoretical density contours refer to non-vibrating atoms[‡].

6.5. *Dipole Moments of Molecules*

In concluding this part of the review, some brief comments are called for on electric dipole moments of molecules. Two calculations of dipole moments have been made so far by the TF method ; for ICl (Glazer and Reiss 1953) and for the C–H bond in methane (Glazer and Reiss 1955). The latter dipole, while of considerable interest, is not directly observable, the resultant dipole moment of the symmetrical methane molecule being of course zero, and none of the comments made below apply to this case. However, for ICl a non-zero value, 0·3 Debye units in the correct sense, was obtained.

[†] An excellent summary of this work has been given by Robertson (1953).

[‡] *Note added in proof.*—Very recently some further calculations along similar lines to those carried out by the present writer have been reported (Cochran, W., 1956, *Acta Cryst.*, 9, 924) in a form comparable with experimental results for salicylic acid. Fairly good agreement is found.

Since this calculation was reported, Brinkman and Peperzak (1955) claim to have shown that the TF method gives a zero value for the dipole moment of any molecule†. Evidently, this claim is in disagreement with the numerical calculations on ICl. Whilst the details of the proof of Brinkman and Peperzak are open to criticism,‡ it seems hard to escape the conclusion that their claim is correct, and that the centroids of the positive and negative charges always coincide. Brinkman and Peperzak also found in their work on H_2O that very slight changes in the electronic distribution give rise to relatively large differences in the values of the dipole moment as found by numerical integration. It seems not impossible that this is the explanation of the non-zero value obtained for ICl, but a more careful investigation is required before a final decision can be reached.

§ 7. SOLIDS

7.1. *Perfect Crystals*

The most detailed calculations for perfect crystals involving the ideas of the statistical theory are those carried out by Gombás and his collaborators. However, a thorough discussion of most of this work is already available in Gombás' book (1949), and for a brief summary of the more recent contributions, together with the relevant references, the article by Löwdin (1956) in this Journal on the 'Quantum Theory of Cohesive Properties of Solids' may be consulted. Therefore we shall not consider this approach here, although it should be noted that results in remarkably good agreement with experiment have been obtained.

We shall confine ourselves to a discussion of methods, initiated by Slater and Krutter (1935), which are based directly on the TF and TFD equations, and much of the treatment will be immediately applicable when solids under extremely high pressures are considered in § 8. While it is undoubtedly true that in its unmodified form (to be contrasted, for example, with the modifications of the statistical approach of Gombás and his co-workers) the usefulness of the method is very limited when dealing with solids under normal conditions, since, of course, it is not capable of accounting for the periodic properties of the elements, it is most useful when the application of high pressures obliterates the detailed influence of the outer electronic structure.

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† The more general claim made by them in this paper has now been withdrawn.

‡ For example, they invoke the result that the electrostatic potential $V \sim r^{-4}$ for large r, which automatically excludes the possibility of a dipole moment.

In principle, the problem of describing the electronic distribution and the field in a crystal in the TF theory can be reduced immediately to that of solving the TF or TFD equations within the cellular polyhedron surrounding a particular atom in the crystal, subject to the condition of periodicity, which amounts to the requirement that the normal derivative of the potential shall vanish over the surface of the atomic polyhedron. Unfortunately, even this problem is much too difficult at present and almost all progress has come from the use of the ‘ sphere approximation ’ (see however § 7.1.4), in which the atomic polyhedron is replaced by a sphere of equal volume, as suggested by Slater and Krutter (1935) in their original paper on the TF method for metals. The problem then reduces to that of solving the dimensionless TF eqn. (4.2), subject to the boundary conditions

$$\phi(0)=1, \quad \frac{\phi(x_0)}{x_0}=\left(\frac{d\phi}{dx}\right)_{x_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (7.1)$$

where x_0 is the radius of the atomic sphere in dimensionless units. Such a solution is shown in curve III of fig. 1. The second boundary condition follows from the periodicity requirement that the gradient of the potential shall be zero across the surface of the atomic sphere, which also automatically ensures charge neutrality. Thus, for any particular element, we can obtain a set of solutions of the TF or TFD equations corresponding to different lattice constants.

We should now like to know whether this method can explain the cohesion of solids. We wish therefore to obtain the derivative of the energy with respect to the radius of the atomic sphere, and the easiest way to calculate this is to compute the pressure p and then use the thermodynamic relation

$$p=-\frac{dE}{dv}=-\frac{1}{4\pi R^2}\frac{dE}{dR} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (7.2)$$

where v is the atomic volume, R is the radius of the atomic sphere $(=bx_0)$ and E is the energy. The pressure p may be obtained intuitively by noting that since the TF theory may be derived by applying free electron relations locally, the pressure due to the bombardment of the electron gas on the boundary of the atomic sphere would then appear to be that due to a free electron gas equal in density to the actual electron gas at the boundary. If $n(R)$ is the boundary density obtained by solution of the TF equation, the pressure is then easily shown to be

$$p=\tfrac{2}{3}c_k\{n(R)\}^{5/3}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (7.3)$$

a result which can be verified rigorously without difficulty. We see from (7.3) that the pressure is never zero, except when $n(R)=0$, which is only true for the isolated atom solution corresponding to an infinite value of R. It is clear then immediately that there is no minimum in the energy curve for the unmodified TF case, as was first shown by Slater and Krutter.

Introducing exchange, arguing intuitively as before, but treating the free electron gas by the Hartree Fock approximation, the pressure p is now given by

$$p=\tfrac{2}{3}c_k\{n(R)\}^{5/3}-\tfrac{1}{3}c_e\{n(R)\}^{4/3}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (7.4)$$

where $n(R)$ is the boundary density calculated from the TFD equation. The expression (7.4) has been the source of considerable confusion, which has arisen because of the difficulties of interpretation in the TFD theory, already discussed fully in § 4. As we saw there, Jensen (1935) proposed that the radius of the ' isolated atom ' be found by minimizing the TFD energy with respect to the radius, and he thus obtained the result embodied in eqn. (7.4). Jensen's proposal, however, is confronted immediately with the difficulty that the ' atom ' has a discontinuity of charge density on the boundary, a state of affairs which conflicts with fundamental wave-mechanical principles. It seems clear to the reviewer that any solution conforming to the periodicity requirement $(dV/dr)_R=0$, with R finite, is leading physically to a description of a crystal, and not to an isolated atom.

7.1.1. *Cohesion of the alkali metals*

As the writer pointed out recently (March 1954 b), the condition that $p=0$ in eqn. (7.4) should give therefore the equilibrium lattice constants of the TFD model for metals. Then the difficulties of the previous interpretation disappear, for whereas Jensen's ' atom ' has a discontinuity in the charge density at the boundary, in the metal model there is no difficulty ; the density in the atomic polyhedron in question (replaced for reasons of mathematical simplicity by a sphere in this treatment) joins smoothly with the density in the neighbouring polyhedra†.

However, since it is evident that the results of the TFD model are applicable, at most, to one group of metals (due to the failure of the statistical theory to account for periodic properties) the question of the correct interpretation arises. It seems clear that the assumptions of the TF method are best fulfilled by the alkali metals (see, for example, Seitz 1940) and everything points to the fact that we ought to compare the theoretical predictions of the model with experimental results for this group. Values of R, say R_e, calculated from eqn. (7.4) with $p=0$ are given in table 6‡. It will be seen that the agreement with experiment is quite gratifying, especially when it is considered that the whole alkali series is dealt with in a general, and entirely non-empirical, manner. It is not, of course, to be supposed that such energy calculations can match in accuracy those made, for example, by the Wigner–Seitz method. However, one attractive feature of the present, admittedly over-simplified, treatment is that the total energy per atom of the crystal is dealt with immediately in a direct manner, whereas in the Wigner–Seitz scheme it is built up as a sum of terms, usually calculated relatively independently.

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† A further point in favour of the writer's views, and against Jensen's interpretation, is that the momentum distribution of electrons corresponding to the TFD solution defined by the zero pressure requirement is characteristic of a metal (see § 7.1.2), and not of an isolated atom.

‡ Very detailed tables of the solutions of the TFD equation corresponding to zero pressure have been given by Thomas (1954), together with values of the various energy terms.

Table 6. Lattice Constants of Alkali Metals

	Li	Na	K	Rb	Cs
TFD R_e (Å)	1·86	2·16	2·28	2·39	2·50
Experiment	1·70	2·09	2·58	2·77	2·98

That the energy curves are not very accurate, in spite of the fact that the positions of the minima are given approximately correctly, is shown by calculating the compressibilities. These do not vary much, but probably decrease slightly, with atomic number. They are all of the order of 50×10^{-12} cm²/dyne, whereas the experimental values range from $(7–50) \times 10^{-12}$ cm²/dyne, through the series from Li to Cs. No calculation of cohesive energy can be made from the present scheme, as there is no acceptable isolated atom. But, in any case, apart from the other approximations involved, correlation energy is entirely neglected and this is now known to contribute very significantly to the binding energies.

Finally, we should emphasize that the above discussion has been given in some detail largely in an attempt to clarify the interpretation of the results of the TFD theory. Further, the general method outlined here has more importance at high pressures, and eqns. (7.3) and (7.4) can then be applied to obtain very useful approximations to the equations of state of solids (see § 8).

7.1.2. *Momentum distribution of electrons in metals*

Before passing on to deal with solids under high pressures, a further application of the TF method to metals under normal conditions is of interest, namely the calculation of the momentum distribution of electrons in metals (March 1954 a). Here the statistical treatment seems to provide a useful approach to a problem which has not hitherto been considered in any detail. Briefly, the importance of the momentum distribution lies in the fact that it determines the shape of the Compton profile in x-ray scattering. From the simple theory of a collision between a photon and a stationary electron, a single modified wavelength λ_c is obtained, given by

$$\lambda_c = \lambda_i + (2h/mc)\sin^2 \tfrac{1}{2}\theta \quad . \quad . \quad . \quad . \quad . \quad . \quad (7.5)$$

where λ_i is the incident wavelength, θ is the angle of scattering and c is the velocity of light. However, when the motion of the electrons in the scatterer is taken into account, there is a kind of Doppler effect, and the momentum distribution can be found from the measured Compton profile. If J is the intensity of the Compton line at a displacement l from the Compton wavelength λ_c, then all scattering angles and incident wavelengths may be included by introducing a variable q defined by

$$q = cl(\lambda_c^2 + \lambda_i^2 - 2\lambda_c\lambda_i \cos\theta)^{-1/2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (7.6)$$

The function $J(q)$ is then given in terms of the momentum distribution function $I(p)$, defined such that $I(p)dp$ is the probability of finding an electron in the solid with momentum of magnitude between p and $p+dp$, by the equation

$$J(q) = \frac{1}{2}\int_q^\infty \frac{I(p)}{p}\,dp. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7.7)$$

Experimental results giving the intensity distribution in the Compton line for metals have been obtained as yet only for Li (Kappeler 1936) and Be (Dumond 1933), and very broad profiles were found, compared with those calculated wave-mechanically for isolated atoms. The problem of understanding these results was first tackled by the TF approximation (March 1954 a), and very recently for Li by a more accurate method (Donovan and March 1956).

The method of calculating $I(p)$ from the TF and TFD models will now be considered. Making use of the fact that the density of states in momentum space is constant, and considering the electrons around the point $\mathbf{r}$, the probability of an electron at $\mathbf{r}$ having momentum of magnitude between p and $p+dp$ is

$$4\pi p^2 dp/\tfrac{4}{3}\pi p_0^3(\mathbf{r}),$$

where at $\mathbf{r}$, the momentum space is occupied up to a maximum momentum $p_0(\mathbf{r})$. Thus the number of electrons between r and $r+dr$, having momenta in the range p to $p+dp$ is

$$\begin{aligned} &3p^2 dp\, n(r) 4\pi r^2 dr/p_0^3(r) \\ &= 32\pi^2 p^2 r^2 dp\, dr/h^3, \end{aligned}$$

since the number of electrons per unit volume at r is $(8\pi/3h^3)p_0^3(r)$. What is required is the probability of an electron lying between p and $p+dp$, irrespective of r, and to facilitate the calculation of this we show in fig. 15 the (r, p) plane for the TF or TFD models. We know that for any value of r, the maximum allowed momentum is $p_0(r)$, and this is determined by the density $n(r)$ calculated from the TF or TFD theories. Thus a curve shown in fig. 15 is defined, dividing the (r, p) plane, and for a fixed p we must clearly integrate from $r=0$ to the value of r defined by this curve. Evidently it is convenient to deal with two regions separately, $p<p_0(R)$ and $p>p_0(R)$. We have then for $p<p_0(R)$

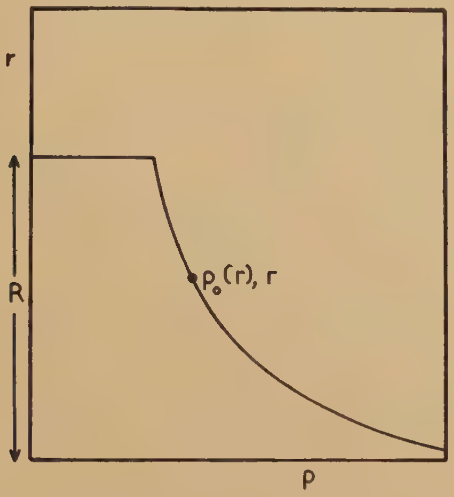
$$\begin{aligned} I(p)dp &= \frac{32\pi^2 p^2 dp}{h^3 Z}\int_0^R r^2 dr \\ &= 32\pi^2 R^3 p^2 dp/3h^3 Z \quad . \quad . \quad . \quad . \quad . \quad . \quad (7.8) \end{aligned}$$

and for $p > p_0(R)$ we must replace the upper limit R by the value of r obtained from the solution of the equation

$$n(r) = (8\pi/3h^3)p^3(r). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7.9)$$

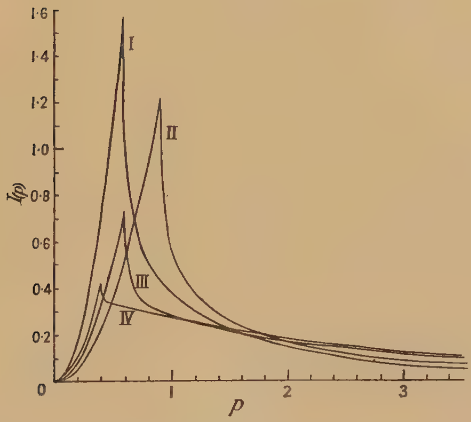
Hence, from a knowledge of $n(r)$, which in turn is found by solving the TF or TFD equations, the function $I(p)$ is easily obtained.

Fig. 15



(r, p) plane for the TF or TFD models.

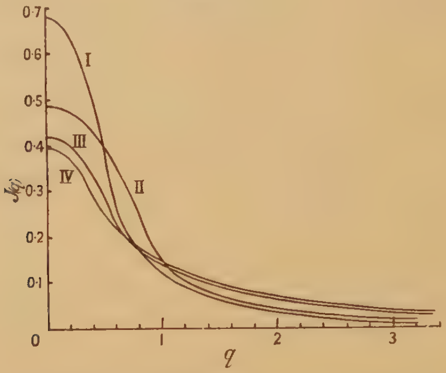
Fig. 16



Momentum distribution function $I(p)$ (atomic units used). I Li ; II Be ; III Na ; IV Na including exchange.
(From March 1954 a.)

Figure 16 shows the results thus obtained for the momentum distribution function $I(p)$ for Li, Be and Na, and the corresponding Compton profiles are shown in fig. 17. Curves I, II and III are calculated from the TF model discussed earlier, and the lattice constants have been taken from experiment. Curve IV is for Na, and shows the effect of exchange; this is the result of using the solution of the TFD equation corresponding to zero pressure discussed earlier. It will be seen that the effect of exchange on the momentum distribution is rather marked in this scheme, although as fig. 17 shows, the Compton profile is not changed very much. The total widths of the profiles at half maximum provide a convenient means of comparison with experiment and are recorded in table 7. Also entered in table 7 are results obtained for K and Rb using the solutions of the TFD equation corresponding to zero pressure.

Fig. 17



Compton profiles (atomic units used).
I Li; II Be; III Na; IV Na including exchange.
(From March 1954 a.)

Table 7. Half Widths of Compton Profiles (in atomic units)

	Li	Be	Na	K	Rb
TF	1·08	1·61	1·30	—	—
TFD	—	—	1·40	1·65	2·11
Isolated atom	0·57	0·77	0·80	1·06	—
Experiment	2·6	2·0	—	—	—

It will be seen that while a marked broadening of the Compton line is predicted when atoms are bound in a lattice, the quantitative agreement between theory and experiment is poor in the case of Li. Surprisingly enough, the result is much better for Be, for the assumptions of the TF theory would seem to be less good in this case. However, it should be borne in mind that the experimental lattice constant has been put into the theory, and the resulting momentum distribution may not be too unrealistic.

In view of the discrepancy between theory and experiment for Li, a more accurate calculation of the momentum distribution has been carried out for this case by Donovan and March (1956). The momentum eigenfunctions of the valence electrons were calculated using the wave function of Seitz (1935) and the result was in good agreement with that given by the TF approximation. Use of a refined wave function obtained by Kohn (1954) leads to virtually no change in the position, and it appears that there is a real discrepancy between theory and experiment. More experimental work in this field would clearly be very valuable.

7.1.3. *Effect of binding on X-ray scattering factors*

A further application of the TF electron densities for crystals is to calculate the difference to be expected between the x-ray scattering factor for an isolated atom and an atom, assumed non-vibrating, bound in a crystal (Umeda and Tomishima, 1953 a, 1955). Whilst the results are of some interest, we shall not go into detail here, as the essential conclusion to be drawn from the calculated scattering factors is that only for light atoms ($Z < \sim 10$) will the influence of binding in a crystal be significant. Unfortunately, for such light atoms it is known that scattering factors calculated from the statistical theory are not satisfactory. For heavier elements, it should be sufficient to use the scattering factors for free atoms. In this connection it is worth remarking that the TF density for isolated atoms is useful when $Z > \sim 20$, and Umeda and Tomishima give more accurate TF scattering factors for isolated atoms than have been available hitherto.

7.1.4. *Attempt to include angular terms in the TF potential*

The work so far considered has been based on the ‘ sphere approximation ’. However, in cases where the cellular polyhedron is not well approximated by a sphere, the angular terms in the potential within the polyhedron may be of some importance. The writer has made an attempt to estimate the size of the angular terms for a diamond-type crystal, in which the polyhedron does indeed deviate rather markedly from a sphere (for a drawing, see Kimball 1935), and preliminary numerical results for Si were reported at a Symposium on ‘ Band Structure ’ held in 1954 at the Radar Research Establishment, Malvern. The method used should be of rather general applicability and we shall therefore briefly outline it in spite of the fact that final numerical results are not available. The terms which occur in the expansion of the potential in lattice harmonics can be obtained from group theory, and the appropriate results for the diamond-type structure are given by Bell (1954). The lattice harmonic we wish to consider is of the form

$$(xyz/r^3)$$

and we attempt to obtain an approximate solution of the TF eqn. (2.5) by writing

$$V-V_0 \doteqdot \frac{Ze}{r}\phi_0+\frac{xyz}{r^3}\cdot\frac{Ze}{r}\phi_3, \quad . \quad . \quad . \quad . \quad . \quad . \quad (7.10)$$

where ϕ_0 and ϕ_3, which are functions only of r, are to be determined. It can then be shown that ϕ_0 and ϕ_3 are approximately given by the solutions of the simultaneous differential equations

$$\frac{d^2\phi_0}{dx^2}=\frac{\phi_0^{3/2}}{x^{1/2}}\left[1+\frac{1}{280}\left(\frac{\phi_3}{\phi_0}\right)^2\right] \quad . \quad . \quad . \quad . \quad . \quad . \quad (7.11)$$

$$\frac{d^2\phi_3}{dx^2}=\left[\frac{12}{x^2}+\frac{3}{2}\left(\frac{\phi_0}{x}\right)^{1/2}\right]\phi_3, \quad . \quad . \quad . \quad . \quad . \quad . \quad (7.12)$$

where x is the customary TF dimensionless variable. Expressing the boundary conditions in terms of the ϕ's we must have $\phi_0(0)=1$, and from eqn. (7.12) it can be shown that for small $x, \phi_3 \propto x^4$. The other conditions must be derived from the periodicity requirement that the normal derivative of the potential across the surface S of the polyhedron is zero, that is

$$\left(\frac{\partial V}{\partial n}\right)_S=0.$$

The major problem was to choose ϕ_0 and ϕ_3 to satisfy this condition as well as possible. After some investigation based on the two-dimensional TF model due to Lennard-Jones and Woods (1928), for which the exact solution is known when the basic ' cell ' is a square, it was decided that a suitable method was to minimize the integral

$$I=\int\left(\frac{\partial V}{\partial n}\right)^2 dS,$$

the integral being taken over the surface of the polyhedron. The calculations are then practicable, if laborious, and preliminary results are available (March 1954 c). One result which can be stated with some certainty, however, is that even in this case, where the cellular polyhedron differs appreciably from a sphere, the simple treatment of Slater and Krutter based on the replacement of the polyhedron by a sphere of equal volume gives a good approximation to the spherical term in the potential. Whilst preliminary results have been obtained for the f-term by the method outlined here, it appears from the writer's calculations that the g-term is also of importance and further work is thus required.

It does seem however that this type of approach, in conjunction, for example, with the variational technique of Jenkins and Pincherle (1954), might be useful in estimating the importance of angular terms in the potential in band structure calculations made by the cellular method. The preliminary calculations of the magnitude of the angular terms make it appear possible that they could be of some importance in the case of Si, but as yet no calculations of the effect on the band structure have been attempted.†

7.2. *The Perturbed Lattice*

Many interesting problems in solid state physics now require an understanding of the perturbations caused in an originally perfect lattice by impurity atoms, missing atoms or vacancies, interstitials and dislocations. We shall mainly be concerned with the work which has been done since the review by Friedel (1954) in this Journal, in which the TF approximation formed the basis of his treatment of the whole subject of impurities in metals. Also, we shall consider the problem of impurities in semiconductors using the generalized TF method, as discussed very recently by Dingle (1955) and Mansfield (1956 a).

7.2.1. *Fields round impurities in monovalent metals*

Following Mott (1936) (see also Mott and Jones 1936) we consider the introduction of a foreign atom, with $Z+1$ electrons outside a closed shell, into a monovalent metal. We treat the conduction electrons by the free electron model, neglecting exchange and correlation, and we wish to find the perturbing potential V_P resulting from the presence of the impurity. Z may be either positive or negative, and we may note at this stage that the case of a vacancy can be included in the present treatment by regarding it as an impurity atom with zero valency, that is corresponding to $Z=-1$ for a monovalent metal. If E_M is the Fermi energy in the unperturbed metal, then the number of electrons per unit volume is given by‡

$$n_0=(2^{3/2}/3\pi^2)E_M^{\,3/2}, \qquad (7.13)$$

and this is also the density of positive charge in the free electron model. For the perturbed lattice§ we have that the modified electron density $n(\mathbf{r})$ is

$$n(\mathbf{r})=(2^{3/2}/3\pi^2)(E_M+V_P)^{3/2}. \qquad (7.14)$$

The resultant charge density at any point is clearly n_0-n, and from Poisson's equation we have therefore

$$\begin{aligned}\nabla^2 V_P&=-4\pi(n_0-n)\\ &=\frac{2^{7/2}}{3\pi}\left[(E_M+V_P)^{3/2}-E_M^{\,3/2}\right]. \qquad (7.15)\end{aligned}$$

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† For the most recent calculations of the band structure of Si by the cellular method, using a spherically symmetrical potential, see Jenkins (1956).

‡ We shall use atomic units throughout this section, unless otherwise stated explicitly.

§ In the case of a finite concentration of impurities, account should be taken of the change in the Fermi level (Friedel 1954, see also Alfred and March 1955). We confine ourselves here to a consideration of a single impurity in an infinite metal.

This equation determines the perturbing potential V_P in the present model when solved subject to the boundary conditions

$$\left.\begin{aligned} V_P &\to \frac{Z}{r} \quad \text{as} \quad r \to 0 \\ V_P &\to 0 \quad \text{as} \quad r \to \infty \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (7.16)$$

Mott obtained an approximate solution in his original paper by linearizing this equation. The basis for this is the assumption that $E_M \gg | V_P |$, which evidently cannot be correct near the point charge. However, making this approximation, eqn. (7.15) reduces to

$$\nabla^2 V_P = \frac{2^{5/2}}{\pi} E_M{}^{1/2} V_P = q^2 V_P \quad . \quad . \quad . \quad . \quad . \quad (7.17)$$

and the solution with spherical symmetry which tends to zero at infinity may be written

$$V_P = \frac{Z\alpha}{r} \exp(-qr) \quad . \quad . \quad . \quad . \quad . \quad . \quad (7.18)$$

where α is the remaining constant of integration. Mott's argument amounts now to using (7.18) over all space, and then from the boundary condition at the origin we must have $\alpha = 1$. It will be seen, however, that strictly (7.17) and (7.18) are valid only for large r, and we shall see later that α appearing in this asymptotic solution depends on Z. However, (7.18) with $\alpha = 1$ shows that the conduction electrons rearrange themselves in order to screen out the field of the point charge, the screening radius $1/q$ being of the order of 1 Å.

Friedel (1954) suggested a method of improving on the linearization or first order approximation, and recently Fujiwara (1955) and Alfred and March (1955) have independently reported results obtained by solving (7.15) exactly by numerical methods for various cases. Fujiwara, in fact, gave results for Cu with $Z=1$, and for Ag with $Z=1$ and 2, while Alfred and March restricted their attention to Cu but dealt with the cases $Z=1$, 2, 3 and 4. The potentials thus obtained for Cu are shown in fig. 18, where the result of the first order approximation is also shown for comparison. Applications of these results, all for positive Z it will be noted, will be discussed shortly, but first of all it is of interest to consider negative values of Z, for which a rather different treatment is required. The simple approximate solution given below is due to Alfred and March (1956).

For this case, we must take account of the fact that in the TF theory no electrons are allowed in regions of negative kinetic energy. Since the potential becomes negatively infinite as the origin is approached, it is clear that we have a sphere, of radius r_c say, surrounding the negative point charge, in which there are no electrons and hence an unneutralized positive charge of density n_0. The radius r_c is determined by the condition

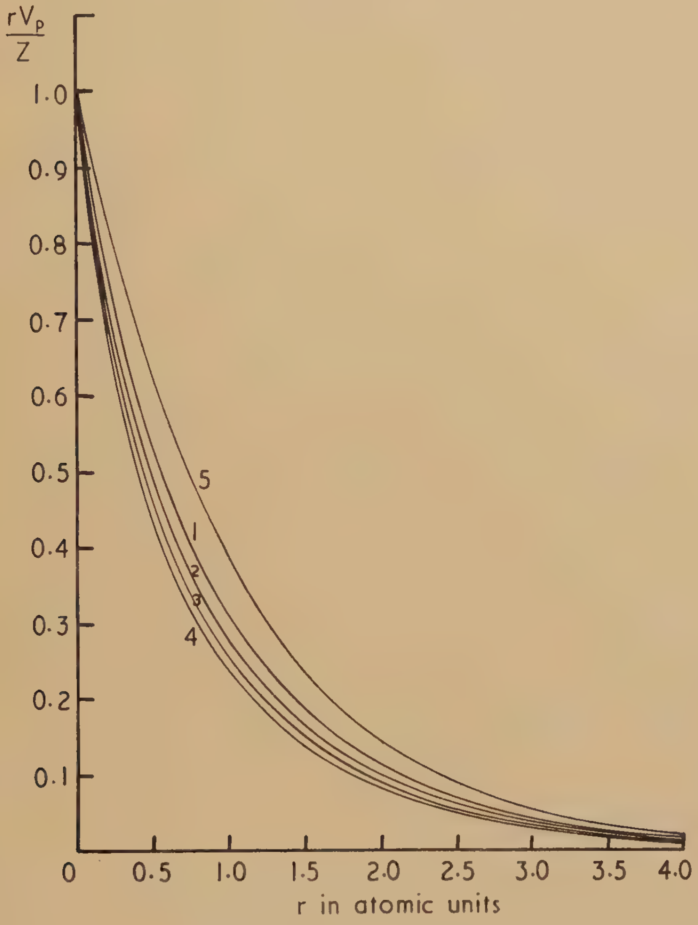
$$-V_P(r_c) = E_M . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7.19)$$

Inside the sphere the potential can easily be obtained ; it is given by

$$V_P = \frac{Z}{r} + \beta - 2^{5/2} E_M{}^{3/2} r^2 / 9\pi \quad . \quad . \quad . \quad . \quad (7.20)$$

where β is a constant of integration. In the outer region, it is assumed that the asymptotic solution (7.18) can be used, and the unknown constants

Fig. 18



rV_P/Z for impurities in copper.
Curves 1 to 4. $Z=1$, 2, 3 and 4 respectively.
Curve 5. First order results.
(After Alfred and March 1955.)

are determined by requiring that the potential and the field shall be continuous at r_c. α and r_c can then be found by solving the equations

$$\left.\begin{aligned} -E_M\left(q+\frac{1}{r_c}\right) &= \frac{Z}{r_c^2} + \frac{4}{9\pi}(2E_M)^{3/2} r_c \\ -Z\alpha \exp(-qr_c) &= r_c E_M \end{aligned}\right\} \quad . \quad . \quad (7.21)$$

and the results obtained for Cu and Ag are shown in table 8. A check on this simple method for Cu and $Z=-1$ is provided by an exact solution obtained by Alfred and the writer (unpublished work) in another connection; the value obtained for α was 1·5(6), in reasonable agreement with the value given in table 8.

Table 8. α as a function of valence difference for impurities (positive Z) in Cu and Ag

	Z	1	2	3	4
Cu	α	0·77	0·67	0·60	0·55
Ag	α	0·75	0·64	(0·56)	(0·50)

r_c (in atomic units) and α for Cu and Ag for negative values of Z

	Z	—1	—2	—3
Cu	r_c	1·41	2·04	2·49
	α	1·40	1·85	2·34
Ag	r_c	1·66	2·38	2·90
	α	1·49	2·04	2·65

The arguments so far have neglected exchange. Various writers have considered ways of introducing it into the theory (Isenberg 1950, Friedel 1954, Fujiwara 1956). We mention here only that the last-named author has given the most thorough discussion available, and has solved the TFD equation for a divalent impurity in Cu and Ag. His essential result is that the impurity is more effectively screened when exchange is included, in agreement with the conclusions of the earlier workers.

7.2.2. *Applications*

(i) *Resistivity of dilute alloys.* The fields obtained in the manner described above can be used to calculate the effect of the introduction of foreign atoms on the resistivity of a metal. This problem, which was

Table 9. Increase in Resistivity $\Delta\rho$ (micro-ohm cm)

	Partial wave method		Experiment	
Solvent	TF	TFD	Cd in solvent	Zn in solvent
Ag	3·09	2·01	0·38	0·62
Cu	2·50	1·67	0·21	0·34

originally tackled by Mott (1936), has since been considered by a number of workers (Friedel 1954, Blatt 1955 b, Fujiwara 1955, 1956.)

Fujiwara has calculated the increase in resistivity $\Delta\rho$ due to 1 atm % of divalent impurity in Ag and Cu, using the fields obtained by numerical solution of the TF and TFD equations, in conjunction with the method of partial waves. The results thus obtained are given in table 9 where relevant experimental results are also shown. It will be seen that the agreement with experiment is not good, the calculated values of $\Delta\rho$ being considerably too high. Friedel (1954) obtained better results for Zn in Cu by assuming a perturbing potential

$$V_P = \frac{Z}{r}\exp(-qr)$$

and then adjusting q to satisfy the Friedel sum rule (Friedel 1952). This can be stated

$$\frac{2}{\pi}\sum_{l=0}^{\infty}(2l+1)\eta_l = Z, \qquad (7.22)$$

where Z is the excess charge on the impurity centre as usual and η_l is the phase shift of the partial wave of order l for electrons at the Fermi surface. By this method Friedel obtained a value for $\Delta\rho$ of less than 1 micro-ohm cm for 1 atm % Zn in Cu, and he concluded that this value should depend little on the exact form of the perturbing potential provided the phase shifts satisfy (7.22). However, the phase shifts given by Fujiwara are recorded in table 10, and it will be seen that for the TF potential the Friedel sum rule is satisfied rather well (although this is not true for the TFD potential). Thus, if Fujiwara's numerical results are correct, a value for $\Delta\rho$ of 2·5 micro-ohm cm for Zn in Cu can result from a potential giving phase shifts which satisfy the sum rule ; in disagreement with Friedel's conclusion. However Blatt (1955 b) finds good agreement with Friedel's results for impurities with higher valencies (see especially fig. 1 of Blatt's paper) and in view of this it seems that Fujiwara's numerical values for $\Delta\rho$ should be treated with some reserve.

Table 10. Phase Shifts η_l of Partial Waves

Solvent		η_0	η_1	η_2	Friedel sum
Ag	TF	1·1374	0·1349	0·0262	1·064
	TFD	0·8538	0·0599	0·0079	0·676
Cu	TF	1·0705	0·1420	0·0276	1·041
	TFD	0·8232	0·0736	0·0082	0·691

(ii) *Solute diffusion in metals.* A further field in which the screening of impurities by the conduction electrons appears to play a fundamental role is that of solute diffusion in metals. The theory, due to Lazarus

(1954, 1955), accounts for the changes in activation energy H and frequency factor D_0 in the equation

$$D=D_0 \exp(-H/RT), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7.23)$$

where D is the measured diffusion coefficient, R is the gas constant and T is the absolute temperature, in terms of the interaction energy between an impurity and a vacancy. This is computed very simply by Lazarus, by neglecting kinetic energy changes and dealing only with the electrostatic interaction of the impurity, represented by a screened potential, and the vacancy. The interaction energy is attractive and of magnitude E_c given by

$$E_c(r)=\frac{Z}{r}\exp(-qr)\,; \quad q^2=\frac{2^{5/2}}{\pi}E_M{}^{1/2}, \quad . \quad . \quad . \quad (7.24)$$

if the first order TF approximation is used. The theory of Lazarus, for full details of which the original paper must be consulted, then leads to the results

$$H(\text{solute})=H(\text{solvent})-[1-\tfrac{1}{4}(q^2r_0{}^2-5qr_0-5)]N_0E_c(r_0) \quad . \quad . \quad (7.25)$$

$$D_0(\text{solute})=D_0(\text{solvent})$$
$$\times \exp\left\{-\frac{\gamma E_c(r_0)}{k}[(qr_0+1)+\tfrac{1}{4}C(-q^3r_0{}^3+6q^2r_0{}^2+5qr_0+5)]\right\}, \quad . \quad (7.26)$$

the latter result being subject to a more drastic approximation than is made in the calculation of H. Here r_0 is the nearest-neighbour distance, N_0 is Avogadro's number, γ is the coefficient of linear expansion, k is Boltzmann's constant, and C is a constant to be evaluated from the observed value of D_0 for self diffusion (for Ag Lazarus calculates C to be 3).

The results of the Lazarus theory for the activation energies for solute diffusion in Ag are shown in fig. 19 and it will be seen that the general trend of the experimental results is satisfactorily shown. More recently, Blatt (1955 a) has attempted to improve the accuracy of the theory by a more accurate calculation of the fields around the solute atoms. Following Friedel he adopted the form

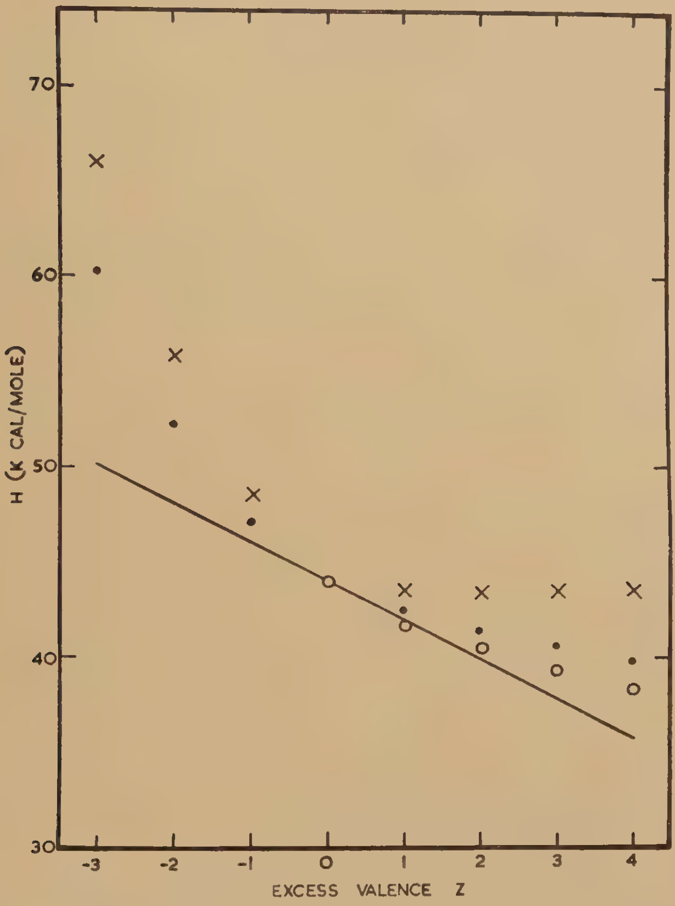
Table 11. Variation of q' with Z for Impurities in Ag

Z	-3	-2	-1	1	2	3	4
$1/q'$ (Å)	0·73	0·7	0·665	0·5	0·485	0·473	0·468

$$V_P=\frac{Z}{r}\exp(-q'r) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7.27)$$

for the potential, and adjusted q' so that the screening charge has its correct value. This leads to a variation of q' with Z, the results being given in table 11. However, the activation energy then turns out to vary much less with Z, when Z is positive, and the agreement is spoilt. As Blatt also emphasized, the screening theory for negative Z predicts a much greater variation of H than for positive Z in this approximation, as can be seen from fig. 19. However, if instead of (7.27), the potentials found by direct numerical solution of the TF equation are used in an attempt to improve the accuracy of the treatment, the agreement with experiment is regained (Alfred and March 1956). The results obtained by numerical solution of the TF equation may be introduced very simply into the theory by noting that it is the potential of the impurity at

Fig. 19



Calculated and experimental activation energies for solute diffusion in silver. —Result of Lazarus, taking $q=1\cdot70$ Å^{-1} ; × results of Blatt ; ● results of Alfred and March ; ○ experimental results.

(From Alfred and March 1956.)

a distance of around 5 atomic units that enters the theory and here the potential is accurately represented by the asymptotic solution

$$V_P = \frac{Z\alpha}{r} \exp(-qr)$$

where α depends on Z and may be obtained from the numerical solutions; the values being recorded in table 8 for Cu and Ag. Thus, the screening depends on Z through α rather than through q, and the activation energies thereby obtained are also shown in fig. 19.

A further consequence of the theory is that a correlation exists between the frequency factor D_0 and the activation energy H, as found experimentally in Ag (Tomizuka and Slifkin 1954) and also in Ni (Swalin and Martin 1954). While the application of the theory to Ni is not likely to lead to quantitative agreement, it is of interest to examine whether the form of the correlation is correctly given by Lazarus' theory and as Swalin (1956) has pointed out the difficulty concerning the proper choice of valences can be avoided by eliminating Z between eqns. (7.25) and (7.26). It is then easily shown that

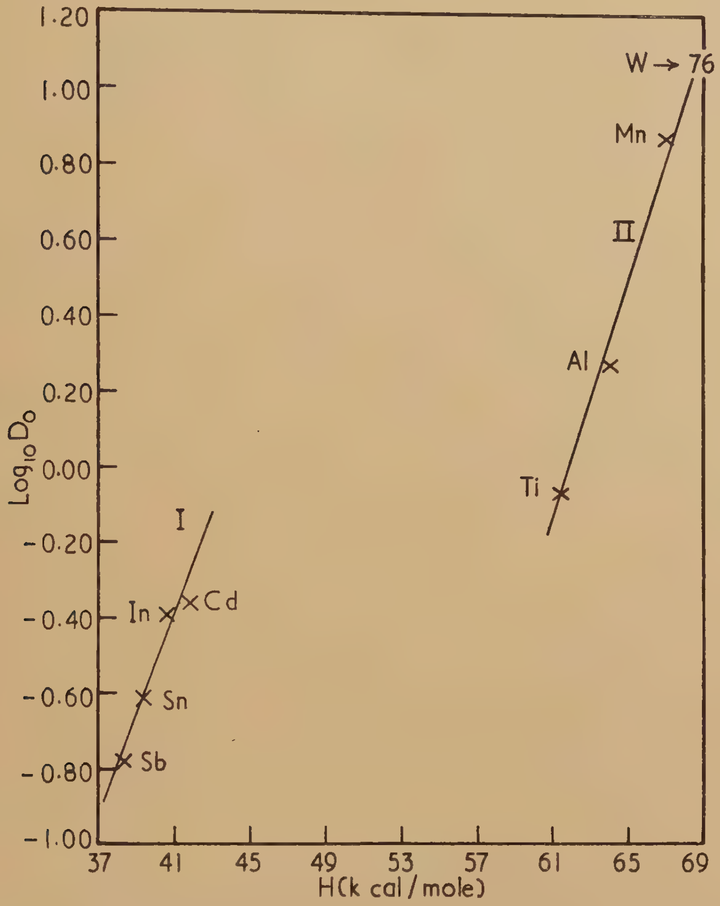
$$\log_{10} D_0 = \left(\frac{\gamma}{2{\cdot}3R}\right) \frac{(1+qr_0)+(\tfrac{1}{4}C)(-q^3r_0^3+6q^2r_0^2+5qr_0+5)}{[1-\tfrac{1}{4}(q^2r_0^2-5qr_0-5)]} H + \text{const.} \qquad \text{(7.28)}$$

Figure 20 shows the experimental results for Ag and Ni plotted in this way, and it will be seen that the predicted linear relation is obeyed quite well in both cases. The slope predicted theoretically for Ag is $8{\cdot}6 \times 10^{-5}$, and if, following Swalin, q is assumed to be the same for Ni as for Ag, a value $4{\cdot}8 \times 10^{-5}$ follows in this case. The experimental slopes calculated from fig. 20 come out to be 13×10^{-5} for Ag and 27×10^{-5} for Ni. The agreement is fairly good therefore for Ag, and even for Ni theory and experiment agree to well within an order of magnitude. It may be remarked here that if Lazarus' theory is modified as suggested by Alfred and March (1956), the result (7.28) is left unchanged, whereas in any treatment in which q varies with Z this will not be so.

Finally, it will be realized that Lazarus' theory is based essentially on a very simple estimate of the interaction between an impurity and a vacancy in a metal. In particular, changes in kinetic energy and exchange energy are neglected in this treatment and in order to put the theory on a firmer basis a more accurate calculation seems called for. This has been undertaken by Mr. L. C. R. Alfred and the writer, for a divalent impurity and a vacancy in Cu, separated by a distance of 5 atomic units. The basic problem is to obtain a solution of (7.15) for this case, and is somewhat similar to that encountered in discussing a heteronuclear diatomic molecule (cf. § 6.1.2). Preliminary results of the energy calculations using this solution indicate that the kinetic energy change is of significance, but that the magnitude of the interaction energy is in reasonable agreement with the value calculated from (7.24).

(iii) *Other work.* Further applications of the above treatment of impurities in metals have been discussed fully by Friedel (1954) and will therefore not be dealt with here, but we should mention interesting later work on the Knight shift in alloys (Friedel 1955). This involves a consideration of large concentrations of impurities, however, and as the background is thoroughly treated by Friedel (1954) (see also Alfred and March 1955) we must reluctantly refer the reader to these papers for further details†.

Fig. 20



$\mathrm{Log}_{10}D_0$ plotted against H for solute diffusion in Ag (I) and Ni (II). (After Swalin 1956.)

7.2.3. *Distribution of electrons round an edge dislocation in a metal*

The problem of finding the distribution of electrons and the field in the neighbourhood of a dislocation is of considerable interest in the calculation of the changes in the conductivity of metals produced by cold-work and has been discussed by several writers. It is not possible here to deal fully with this difficult problem and we shall content ourselves with a somewhat naive and over-simplified presentation. The result obtained below for the field round a dislocation was first given by Landauer (1951) (in connection with this work, see also Dexter (1952 a, b)).

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† *Note added in proof.*—Reference should also be made to very recent work (Heine, V., 1956, *Proc. Phys. Soc.* A, **69**, 505, 513) on the de Haas–van Alphen effect in alloys and on the band structure of bismuth.

Landauer's starting point was an expression, due essentially to Koehler (1941), giving the relative change in ionic density due to an edge dislocation in a metal. If n_i is the ionic density in the unperturbed metal and the change is denoted by Δn_i, then we have

$$\frac{\Delta n_i}{n_i}=\frac{a}{2\pi}\frac{(1-2\nu)}{(1-\nu)}\frac{\sin\theta}{r}=\frac{\lambda\sin\theta}{r}. \quad . \quad . \quad . \quad . \quad . \quad (7.29)$$

Here cylindrical polar coordinates are used, with the z-axis along the dislocation, θ is the angle measured with respect to the slip plane, a is the lattice spacing of the simple cubic lattice on which the argument leading to (7.29) is based, and ν is Poisson's ratio.

If we describe the conduction electrons in the unperturbed metal by the free electron model and if V_P is the resultant electrostatic potential in the perturbed metal, then the usual relation between the density $n(\mathbf{r})$ and the potential V_P is

$$n(\mathbf{r})=\frac{2^{3/2}}{3\pi^2}(E_M+V_P)^{3/2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7.30)$$

where the Fermi level is assumed unchanged from that of the unperturbed metal. We then find

$$\nabla^2 V_P=\frac{2^{7/2}}{3\pi}\left[(E_M+V_P)^{3/2}-E_M{}^{3/2}\left(1+\frac{\lambda\sin\theta}{r}\right)\right] \quad . \quad (7.31)$$

as the equation to solve for V_P.

This represents a somewhat formidable problem, but sufficiently far from the axis of the dislocation, E_M can be assumed to be much larger than $|V_P|$ and eqn. (7.31) may then be replaced by the approximate form

$$\nabla^2 V_P=\frac{2^{5/2}}{\pi}E_M{}^{1/2}V_P-\frac{2^{7/2}}{3\pi}E_M{}^{3/2}\frac{\lambda\sin\theta}{r}. \quad . \quad . \quad . \quad (7.32)$$

It is now easy to verify that a physically acceptable solution is

$$V_P=\tfrac{2}{3}E_M\frac{\lambda\sin\theta}{r} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7.33)$$

which is just Landauer's result and corresponds to the potential of a line dipole placed along the dislocation axis.

The potential (7.33) may be used to calculate the changes in conductivity produced by cold-work (Landauer 1951, see also Dexter 1952 a, b) and the results obtained are essentially equivalent to those found earlier by Mackenzie and Sondheimer (1950). This equivalence appears to be due to the fact that both are essentially based on the linearized TF equation, and whereas in the treatment outlined here the ionic density is smeared out originally; in the approach of Mackenzie and Sondheimer the conduction electrons screen each positive ion in its displaced position and the ‘ smearing out ’ occurs later in the calculation of the scattering matrix elements.†

The most thorough treatment yet available of the change in conductivity of a metal produced by dislocations is that of Hunter and Nabarro (1953), based on the Wigner–Seitz approximation. For a more complete discussion of the problem than we have been able to give here, the reader should consult this paper, together with the earlier paper by Bardeen and Shockley (1950) on deformation potentials.

7.2.4. *Impurities in semiconductors*

The theory of impurity scattering in semiconductors has a good deal of interest from a practical point of view and can be tackled along rather similar lines to the corresponding problem in metals, although it is fairly evident that a number of modifications must be made. For example, it is no longer permissible to suppose in general that in semiconductors we are dealing with a completely degenerate gas of free electrons, and indeed in many cases the assumption that the electrons obey Maxwell–Boltzmann statistics is more appropriate. This latter case has been discussed by Debye and Conwell (1954) who give a formula for the mobility, derived by Herring. The generalization to arbitrary degeneracy has been considered independently by Dingle (1955) and Mansfield (1956 a).

In order to calculate the field round an ionized impurity centre, use is made of the ‘ generalized TF theory ’, first formulated for low temperatures by Marshak and Bethe (1940) and for arbitrarily high temperatures by Sakai (1942) and, independently, Feynman *et al.* (1949) in the course of their work on equations of state of elements at high pressures and temperatures (see § 8). In this generalized theory, the restriction made in § 2 that the electron gas is completely degenerate is removed and the Fermi–Dirac distribution function must be introduced into the theory.

(i) *Relation between density and potential in the generalized TF theory.*‡ The number of electrons with momenta of magnitude between p and $p+dp$ in a volume element d_τ must now be

$$4\pi p^2 dp d_\tau \frac{2}{h^3} \Big/ \left[\exp\left\{\left(\frac{p^2}{2m^*} - eV\right)\Big/ kT - \eta^*\right\} + 1\right] \quad . \quad (7.34)$$

where V is the electrostatic potential, m^* is the effective electronic mass and η^* is a constant, the reduced chemical potential of the electrons, which is to be determined by normalization requirements. Thus it follows immediately that the electron density $n(\mathbf{r})$ is given by

$$n(\mathbf{r}) = \int_0^\infty \frac{8\pi p^2 dp}{h^3} \Big/ \left[\exp\left\{\left(\frac{p^2}{2m^*} - eV\right)\Big/ kT - \eta^*\right\} + 1\right]. \quad . \quad (7.35)$$

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† The writer wishes to thank Dr. R. Landauer for a very helpful correspondence in connection with the material presented in this section.

‡ It should be noted that we are no longer using atomic units in § 7.2.4.

This is the modified relation between density and potential in the generalized TF approximation. If we introduce the Fermi–Dirac functions $I_k(\eta^*)$ defined by

$$I_k(\eta^*)=\int_0^\infty \frac{y^k dy}{[\exp(y-\eta^*)+1]} \quad . \quad . \quad . \quad . \quad (7.36)$$

then (7.35) becomes

$$n(\mathbf{r})=\frac{4\pi}{h^3}(2m^*kT)^{3/2}I_{1/2}\left(\eta^*+\frac{eV}{kT}\right). \quad . \quad . \quad . \quad (7.37)$$

(ii) *Field round an ionized impurity centre.* We note now that if n_0 is the density of electrons in the unperturbed lattice, then since n_0 is also the density of positive charge, Poisson's equation gives us

$$\nabla^2 V_P=-\frac{4\pi e}{\kappa}(n_0-n) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7.38)$$

where κ is the dielectric constant and V_P is the perturbing potential as usual. Assuming that η^* is unchanged by the introduction of the impurity we have therefore,

$$\nabla^2 V_P=\frac{16\pi^2 e}{\kappa h^3}(2m^*kT)^{3/2}\left[I_{1/2}\left(\eta^*+\frac{eV_P}{kT}\right)-I_{1/2}(\eta^*)\right] \quad . \quad . \quad (7.39)$$

since n_0 is evidently given by

$$n_0=\frac{4\pi}{h^3}(2m^*kT)^{3/2}I_{1/2}(\eta^*). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7.40)$$

For the case of an infinite semiconductor with a single impurity centre at the origin of coordinates we must find a solution with spherical symmetry such that

$$\left.\begin{array}{lll} V_P\to\dfrac{e}{\kappa r} & \text{as} & r\to 0 \\ V_P\to 0 & \text{as} & r\to\infty \end{array}\right\} \quad . \quad . \quad . \quad . \quad (7.41)$$

In order to obtain an approximate solution, Dingle (1955) and Mansfield (1956 a) assume (cf. Mott 1936) that

$$|\eta^* kT|\gg|eV_P|$$

and write (7.39) in the approximate form

$$\begin{aligned}\nabla^2 V_P&=\frac{16\pi^2 e}{\kappa h^3}(2m^*kT)^{3/2}\frac{eV_P}{kT}\frac{\partial}{\partial\eta^*}I_{1/2}(\eta^*)\\ &=q^2V_P. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7.42)\end{aligned}$$

Evidently the solution of (7.42) satisfying the boundary conditions (7.41) is

$$V_P=\frac{e}{\kappa r}\exp(-qr) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7.43)$$

with

$$q^2=\frac{16\pi^2 e^2}{\kappa h^3}(2m^*)^{3/2}(kT)^{1/2}I_{1/2}'(\eta^*).$$

The expression for q^2 reduces, in the completely degenerate case, to

$$q^2 = \frac{16\pi^2 m^* e^2}{\kappa h^2}\left(\frac{3n_0}{\pi}\right)^{1/3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7.44)$$

which is easily shown to be equivalent to q^2 as given by (7.17), if we replace κ by unity, put $m = m^*$, and introduce atomic units. In the non-degenerate case,

$$q^2 = \frac{4\pi e^2 n_0}{\kappa k T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7.45)$$

and as an example to which (7.45) is applicable, taking one impurity P atom for every 10^5 Si atoms, $1/q$, the screening radius, is found to be 57 Å at room temperature.

(iii) *Conductivity due to impurity scattering.* The fields calculated above can be used to derive an expression for the conductivity due to impurity scattering. The only work so far has involved the use of the Born approximation which is known in the case of metals to lead to considerable errors †. We shall simply quote the result obtained by Mansfield; namely that the conductivity σ_I due to impurity scattering may be written, if N_i is the concentration of impurity centres,

$$\sigma_I = \frac{32\kappa^2 m^* (kT)^3}{N_i e^2 h^3 f(\bar{x})} I_2(\eta^*) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7.46)$$

where

$$f(\bar{x}) = \ln(1+\bar{x}) - \frac{\bar{x}}{1+\bar{x}},$$

$$\bar{x} = \frac{\bar{\eta}(kT)^{1/2}\kappa h}{e^2 (2m^*)^{1/2} I_{1/2}{}'(\eta^*)}, \quad \text{and} \quad (\bar{\eta}-3)\exp(\bar{\eta}-\eta^*) = \bar{\eta}+3.$$

It may be remarked here that in addition to the use of the Born approximation, Mansfield evaluates an integral involving $f(x)$ by an approximate method in which $f(x)$ is replaced by its value at a particular argument $\bar{x}$. A somewhat modified procedure for the calculation of $\bar{x}$ which may give rather better results has been proposed by Dingle (1955).

Mansfield has also discussed the conductivity in the case of combined impurity and lattice scattering and has made a comparison with experiment for Ge and InSb; reasonable values for m^* and κ thereby result. Finally it should be mentioned that in a later paper (Mansfield 1956 b) modified results for the Hall constant are also reported.

§ 8. MATERIAL UNDER HIGH PRESSURE

As we emphasized in § 7.1 the TF method is limited in its usefulness when we are dealing with perfect crystals under normal conditions, since it cannot account for the periodic properties of the elements. However, when pressures sufficient to obliterate the detailed influence of the outer electronic structure are applied, the results of the method should be valid for all elements. The information thus obtained on the behaviour of material at high pressures has proved of very considerable value in astrophysics and, to a lesser extent, also in geophysics. It would be outside the scope of the present article to discuss such applications in detail but as examples we might mention the work of Brown (1950) on the compositions and structures of the planets, the calculations of the mass-radius relationship of the planets and the white dwarfs (Sommerfeld 1938, Scholte 1947, see however Ramsey 1950), and the discussions of Elsasser (1951) and Bullen (1952) on the internal constitution of the earth. This latter work will be referred to briefly again in § 8.6.

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† *Note added in proof.*—A thorough investigation of scattering by ionized impurities in semiconductors, in which the Born approximation is avoided and the method of partial waves used, has now been made by Professor F. J. Blatt (private communication) and the results will be published shortly.

We shall confine ourselves here to a consideration of the equations of state of elements as given by the TF and TFD methods ; to the results of generalizing the theory to deal with the high temperatures often encountered in astrophysical problems ; and to the relation between the predictions of the theory and existing experimental information obtained in the laboratory. This information, available to us mainly through the work of Bridgman (1941, 1948, 1949), exists up to pressures of 10^5 atmospheres†, but there is then a considerable gap before the results of the TF model can be trusted. In fact, there is some disagreement with regard to the pressures at which the TF equations of state may be safely applied (see § 8.6). For most purposes it should suffice to use the criterion of Feynman *et al.* (1949), namely that the results will be valid only at pressures exceeding 10^7 atmospheres.

8.1. *Equations of State from the TF Model*

In the completely degenerate case, the equation of state is given in the TF theory by eqn. (7.3), once the boundary density $n(R)$ is known from the solution ϕ of the dimensionless TF eqn. (4.2), subject to the boundary conditions (7.1). From the relation between $n(R)$ and the boundary value of ϕ, $\phi(x_0)$, the pressure p may be conveniently written in the form

$$pv = \frac{2}{15}\frac{Z^2e^2}{b}x_0{}^{1/2}\{\phi(x_0)\}^{5/2}, \qquad (8.1)$$

where v is the atomic volume.

The earliest work in this field was carried out, following a suggestion by Slater and Krutter (1935), by Jensen (1938) and, some years later, by Feynman *et al.* (1949). Recent work by Gilvarry (1954 b) and March (1955 a) has enabled the results to be put into a form which should represent accurately the predictions of the TF theory over the entire pressure range. It should be emphasized that no claim is made regarding the validity of such equations of state over a wide range of pressures ; as already pointed out, it is only when dealing with pressures of the order of 10^7 atmospheres that the results will be at all generally applicable, and even then the effect of exchange should be considered.

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† This range can now be extended somewhat by shock wave measurements (see § 8.6).

The treatment of Gilvarry consisted in examining, first of all, the limiting forms of the equations of state at very high and very low pressures. An approximate form was then found which was correct in these limits and which fitted the available numerical data with fair accuracy in the intermediate regions. The limiting forms, particularly the high pressure case, are of some interest and we shall briefly consider them here. Gilvarry argued intuitively that at sufficiently high pressures the results, for an element of atomic number Z, must go over into those appropriate for a free electron gas, with density corresponding to Z electrons in the atomic volume v. The equation of state may then be written down immediately (see eqn. (7.3)) as

$$pv=\frac{h^2}{5m}\left(\frac{3}{8\pi}\right)^{2/3}\frac{Z^{5/3}}{v^{2/3}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8.2)$$

and this corresponds to a value of ϕ at the boundary of the atomic sphere of radius bx_0 given by

$$\phi(x_0)=3^{2/3}/x_0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8.3)$$

More recently the present writer has discussed how this result follows from the properties of the dimensionless TF equation, and in this way has obtained a further term in a series development of the boundary value $\phi(x_0)$. The result is

$$\phi(x_0)=\frac{3^{2/3}}{x_0}\left[1-\frac{3^{1/3}}{10}x_0+\dots\right], \quad . \quad . \quad . \quad . \quad . \quad (8.4)$$

which leads to the equation of state

$$pv=\frac{h^2}{5m}\left(\frac{3}{8\pi}\right)^{2/3}\frac{Z^{5/3}}{v^{2/3}}\left[1-\frac{2\pi me^2}{h^2}(4Zv)^{1/3}+\dots\right]. \quad . \quad (8.5)$$

The first term is, of course, independent of the electronic charge; the second, involving e^2, shows the way in which the equation of state is modified at the highest pressures by including electron–nuclear and electron–electron interactions by means of the TF theory. It is of interest to note in passing that this equation of state was assumed by Kothari (1936, 1938), on purely intuitive grounds, in his work on the mass-radius relation for the planets; the second term arising from a consideration of the interactions of a uniform distribution of electrons with the nucleus of charge Ze and among themselves. However, as we shall see later, a term of the same order of magnitude in the atomic volume arises from exchange.

For low pressures no simple physical argument exists, but using an asymptotic solution of the dimensionless TF equation (Sauvenier 1939, see also Umeda 1951) Gilvarry has obtained the result that the boundary value $\phi(x_0)$ is given by

$$\phi(x_0)=16(3+2\lambda_1)/x_0^3 \quad . \quad . \quad . \quad . \quad . \quad (8.6)$$

where

$$\lambda_1=\tfrac{1}{2}(\sqrt{73}+7)=7{\cdot}77200,$$

or

$$\phi(x_0)=296{\cdot}70/x_0^3. \qquad (8.7)$$

Gilvarry then proposed the approximate analytical form

$$\phi(x_0)=\left[\sum_{n=2}^{6} A_n x_0^{1/2n}\right]^{-1} \qquad (8.8)$$

to represent the TF results for the boundary value ; A_2 and A_6 being chosen so that the limiting results (8.3) and (8.7) are given correctly. Gilvarry's values for the remaining coefficients, chosen to obtain a good fit with the available numerical data, were slightly modified by the writer in order that (8.8) should reproduce (8.4) for small x_0, and the values of A_n thus obtained are recorded in table 12. The resulting expression for $\phi(x_0)$ then fitted the existing numerical data to better than 1%, although A_5 was the only adjustable parameter. Thus, a convenient representation of the TF equations of state, which should be sufficiently accurate for most purposes, is

Table 12. Coefficients in Fitted Functions for $\phi(x_0)$ and a_2

$\phi(x_0)$		$a_2-a_{2\infty}$	
A_2	$4{\cdot}8075\times10^{-1}$	B_2	$4{\cdot}8075\times10^{-1}$
A_3	0	B_3	$4{\cdot}3462\times10^{-1}$
A_4	$6{\cdot}934\times10^{-2}$	B_4	$6{\cdot}9203\times10^{-2}$
A_5	$9{\cdot}700\times10^{-3}$	B_5	$5{\cdot}9472\times10^{-2}$
A_6	$3{\cdot}3704\times10^{-3}$	B_6	$-4{\cdot}9688\times10^{-3}$
		B_7	$4{\cdot}3386\times10^{-4}$
		B_{λ_1}	$1{\cdot}5311\times10^{-6}$

$$p^{2/5}\left[\sum_{n=2}^{6} A_n\left(\frac{3v}{4\pi b^3}\right)^{(n+2)/6}\right]=\left(\frac{Z^2e^2}{10\pi b^4}\right)^{2/5}. \qquad (8.9)$$

It is also of interest to note that a simple analytic approximation to the total energy, which is the basic thermodynamic function at $T=0$, also exists. As was first shown by Slater and Krutter (1935), the difference between the total energy for finite x_0 and for an isolated atom ($x_0=\infty$) is given by

$$\mathrm{E}(x_0)-\mathrm{E}(\infty)=\frac{Z^2e^2}{b}\left[\tfrac{3}{7}(a_2-a_{2\infty})+\tfrac{2}{35}x_0^{1/2}\{\phi(x_0)\}^{5/2}\right] \qquad (8.10)$$

where a_2 is the slope of ϕ at the origin. a_2 may be written in a convenient form similar to that used for $\phi(x_0)$; namely

$$a_2-a_{2\infty}=\left[\sum B_n x_0^{\,n}\right]^{-1}, \qquad (8.11)$$

where n ranges over the sequence $n=2, 3 \ldots 7, \lambda_1$; B_2 and B_{λ_1} again being chosen to yield the correct asymptotic forms. The values of B_n

given by Gilvarry are recorded in table 12, and thus $E(x_0)-E(\infty)$ is known from (8.8), (8.10) and (8.11). The other thermodynamic functions can be easily obtained if required (see especially Gilvarry 1954 b).

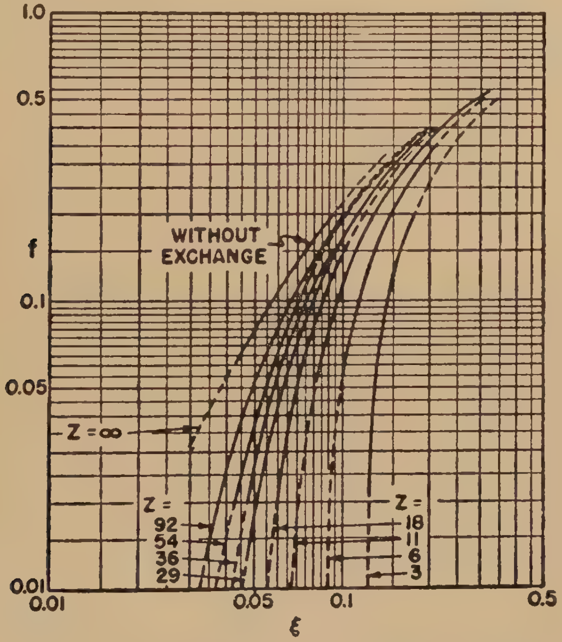
8.2. *Equations of State from the TFD Model*

The eqn. (7.4) in principle defines the equation of state in the TFD approximation, and in terms of the boundary value $\phi(x_0)$ found by solving the TFD equation this may be written

$$pv=\frac{2}{15}\frac{Z^2e^2}{b}x_0^{\,3}\left[\left\{\frac{\phi(x_0)}{x_0}\right\}^{1/2}+\alpha\right]^5\left[1-\frac{5\alpha/4}{\{\phi(x_0)/x_0\}^{1/2}+\alpha}\right]. \qquad (8.12)$$

Unfortunately, the TFD equation must be solved separately for each Z, and as yet no approximate means of expressing the TFD equations of state in an analytical form applicable to all elements has been found. If such a procedure could be devized it would certainly be very convenient from a practical point of view. In general then, the equations of state must be obtained from (8.12) in conjunction with existing numerical solutions of the TFD equation. Of these, the most useful tabulation

Fig. 21



Representation of TFD relations between pressure and density for different atomic numbers. f is related to the pressure and ξ^3 is proportional to the density. (From Feynman, Metropolis and Teller 1949.)

from the present point of view is that of Metropolis and Reitz (1951), but for many purposes the graphical presentation of the equations of state by Feynman *et al.* is adequate, and their results are reproduced in fig. 21. The variables f and ξ which they use, following Jensen, are related to $\phi(x_0)$ and x_0 in (8.12) by the equations

$$\left.\begin{aligned} f(\xi)&=\frac{x_0{}^3}{3}\left[\left\{\frac{\phi(x_0)}{x_0}\right\}^{1/2}+\alpha\right]^3\left[1-\frac{5\alpha/4}{\{\phi(x_0)/x_0\}^{1/2}+\alpha}\right]^{3/5}, \\ \xi&=\frac{Z^{-2/3}a_0}{bx_0}\left(\frac{3Z}{4\pi}\right)^{1/3}=\frac{4}{6^{1/3}\pi x_0}. \end{aligned}\right\} \qquad (8.13)$$

Finally, it is of interest to point out that a general form for the equation of state can be obtained at the highest pressures, to the same order of accuracy as that given in eqn. (8.5) for the TF theory. The result is (March 1955 a)

$$pv=\frac{h^2}{5m}\left(\frac{3}{8\pi}\right)^{2/3}\frac{Z^{5/3}}{v^{2/3}}\left[1-\frac{2\pi me^2}{h^2}(4Zv)^{1/3}-\frac{10\pi me^2}{3^{2/3}h^2}(4Zv)^{1/3}\alpha+\dots\right]. \quad . \quad . \quad . \quad (8.14)$$

This equation demonstrates the effect of exchange on the equation of state at the highest pressures and by substituting for α it is easy to show that the exchange correction is simply the free electron exchange term for Z electrons in a volume v. Apart from its intrinsic interest, (8.14) or the corresponding equation for the boundary value,

$$\phi(x_0)=\frac{3^{2/3}}{x_0}\left[1-\frac{3^{1/3}}{10}x_0-\frac{2\alpha}{3^{1/3}}x_0+\dots\right], \quad . \quad . \quad . \quad (8.15)$$

should be useful in any attempt to set up analytical functions to fit the numerical data for the TFD equations of state.

8.3. *TF Equations of State for the Case of Incomplete Degeneracy*

Thus far it has been assumed that the electrons form a completely degenerate gas. Often, however, in astrophysics, this assumption is not permissible and it is necessary to generalize the method. An account of this generalization has already been given in § 7.2.4. For the low temperature case, first discussed by Marshak and Bethe (1940), results for the equations of state may again be expressed in a convenient approximate analytical form applicable to all elements (Gilvarry 1954 b, Gilvarry and Peebles 1955, March 1955 b)†. For this reason we shall consider these results briefly here, although the discussion in § 8.4 is applicable to arbitrary temperatures and therefore in principle covers the case dealt with here.

If the pressure in the case of incomplete degeneracy is P, then this can be expressed in terms of the pressure p in the completely degenerate case already considered, by the equation

$$P=p[1+\tfrac{5}{2}(\sigma+2\tau)\zeta(kT)^2]. \quad . \quad . \quad . \quad . \quad . \quad . \quad (8.16)$$

---

† See also Marshak *et al.* (1950) for other interesting work involving the method of Marshak and Bethe.

Here
$$\zeta = \pi^2 b^2/8Z^2e^4,$$
τ is defined by
$$\tau\{\phi(x_0)\}^2 = x_0^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8.17)$$
where $\phi(x_0)$ is, as usual, the boundary value obtained by solving the dimensionless TF equation, and σ may be represented approximately by
$$\sigma\phi(x_0) = \sum C_n x_0^n, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8.18)$$
where in the summation, $n=3$, n' and 5. The values of n' and of the coefficients C_n are recorded in table 13†.

Table 13. Coefficients C_n in equation (8.18)

n	C_n
3	$-3{\cdot}205 \times 10^{-1}$
$n' = 4{\cdot}215$	$-2{\cdot}331 \times 10^{-2}$
5	$-2{\cdot}519 \times 10^{-3}$

These results can be used whenever the temperature is low in comparison with the maximum kinetic energy of electrons near the boundary of the atomic sphere, or when the inequality
$$kT \ll \frac{Ze^2}{b}\left[\frac{\phi(x_0)}{x_0}\right] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8.19)$$
is satisfied. As Gilvarry has emphasized, since $\phi(x_0)/x_0 \sim x_0^{-2}$ as $x_0 \to 0$ (cf. eqn. (8.3)), it follows that in this case high temperatures fall within the range of this treatment. Gilvarry (1954 b) has also given a thorough discussion of the various thermodynamic functions in this case and reference should be made to his paper for details.

8.4. *Generalized TF Theory for Arbitrary Degeneracy*

8.4.1. *A generalized variation principle*

We have already outlined a simple argument showing how the relation (7.37) between density and potential in the generalized TF theory is derived. This was essentially the argument given by Feynman *et al.* (1949). However, it is instructive, particularly from the point of view of obtaining the various thermodynamic functions from the theory, to examine whether this relation between density and potential may be derived from a variation principle which is a generalization of that given in § 2, where it was pointed out that the ordinary TF relation (2.3) (valid at $T=0$) can be obtained by requiring that the total energy shall be stationary with respect to variations in the density.

This generalized variation principle is given below. The writer believes that the argument is original and therefore the essential steps will be given. First of all, let us try to set up the free energy in the generalized TF model by making use of the fact that in this theory free electron relations are applied locally.

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† The results given in table 13 are those of Gilvarry and Peebles (1955). Values obtained independently by the writer (March 1955 b) are in excellent agreement with these.

Thus, let us first consider N free electrons enclosed in a volume V at a temperature T. The thermodynamic functions for this case are well known (see, for example Stoner 1939, where the relations are given in a particularly convenient form for the present purpose) and may be written :

Kinetic or internal energy $$E=\tfrac{3}{2}NkT\left(\frac{kT}{\epsilon_0}\right)^{3/2} I_{3/2}(\eta) \quad . \quad . \quad . \quad . \quad (8.20)$$

where $$\epsilon_0=\frac{h^2}{2m}\left(\frac{3N}{8\pi V}\right)^{2/3},$$

and η is defined by the equation

$$1=\frac{3}{2}\left(\frac{kT}{\epsilon_0}\right)^{3/2} I_{1/2}(\eta). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8.21)$$

Entropy $$S=(\tfrac{5}{3}\{I_{3/2}/I_{1/2}\}-\eta)Nk. \quad . \quad . \quad . \quad . \quad . \quad (8.22)$$

Free energy $$\begin{aligned} F&=E-TS \\ &=NkT(\eta-\tfrac{2}{3}\{I_{3/2}/I_{1/2}\}). \quad . \quad . \quad . \quad . \quad (8.23)\end{aligned}$$

This suggests that we set up the free energy in the generalized TF theory by taking the free energy/unit volume from the free electron theory, adding the usual electrostatic potential energy terms and making the density N/V a function of position. We then have

$$F=\int nkT(\eta-\tfrac{2}{3}\{I_{3/2}/I_{1/2}\})d\tau-\tfrac{1}{2}e\int nV_e d\tau-e\int nV_N d\tau \quad . \quad (8.24)$$

where, as usual, V_e and V_N are the electrostatic potentials due to the electrons and nuclei respectively. It will now be shown that if we require F to be stationary with respect to variations in n, subject to the normalization requirement that

$$\int n d\tau=\text{constant},$$

the relation (7.37) between density and potential follows. It will be seen from (8.21) that the variation of F may equally well be carried out with respect to η, and this proves more convenient in fact. We have then

$$\begin{aligned}\delta F=&\int\frac{\partial n}{\partial\eta}kT(\eta-\tfrac{2}{3}\{I_{3/2}/I_{1/2}\})\delta\eta d\tau \\ &+\int nkT\left[1-\tfrac{2}{3}\frac{\{I_{1/2}I_{3/2}'-I_{3/2}I_{1/2}'\}}{I_{1/2}^2}\right]\delta\eta d\tau \\ &-e\int\frac{\partial n}{\partial\eta}V\delta\eta d\tau+eV_0\int\frac{\partial n}{\partial\eta}\delta\eta d\tau \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8.25)\end{aligned}$$

where V_0 is a Lagrange multiplier, and $V=V_e+V_N$. We have not considered the potential energy terms fully here as the result is well known (see, for example, Corson 1951). Now in general we have (McDougall and Stoner 1938)

$$\frac{\partial}{\partial\eta}I_k(\eta)=kI_{k-1}(\eta) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8.26)$$

and in particular

$$I_{3/2}{}'(\eta)=\tfrac{3}{2}I_{1/2}(\eta).$$

Thus, the first two terms in the square bracket of the second integral in (8·25) vanish. Further, it is easy to show from (8.21) that

$$I_{1/2}{}'(\eta)=\frac{I_{1/2}(\eta)}{n}\frac{\partial n}{\partial\eta} \quad . \quad . \quad . \quad . \quad . \quad . \quad (8.27)$$

and then (8.25) becomes

$$\delta F=\int\frac{\partial n}{\partial\eta}kT\eta\delta\eta d\tau-e\int\frac{\partial n}{\partial\eta}V\delta\eta d\tau+eV_0\int\frac{\partial n}{\partial\eta}\delta\eta d\tau. \quad . \quad (8.28)$$

The requirement that δF is zero gives therefore

$$kT\eta-e(V-V_0)=0$$

or

$$\eta=\frac{e(V-V_0)}{kT}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8.29)$$

From (8.21) and (8.29) it therefore follows that

$$n=\frac{4\pi}{h^3}(2mkT)^{3/2}I_{1/2}\left(\frac{eV}{kT}-\frac{eV_0}{kT}\right) \quad . \quad . \quad . \quad (8.30)$$

which is equivalent to the relation (7.37).

Actually, an expression for the free energy which is equivalent to that given in (8.24) was first derived by Brachman (1951) by integration of the Gibbs–Helmholtz equation. That the entropy, and hence the free energy, could be set up by the method used here seems to have been first pointed out by the writer (March 1953 a).

8.4.2. *The generalized TF equation and equations of state*

Combining (8.30) with Poisson's equation, we have the generalized TF equation

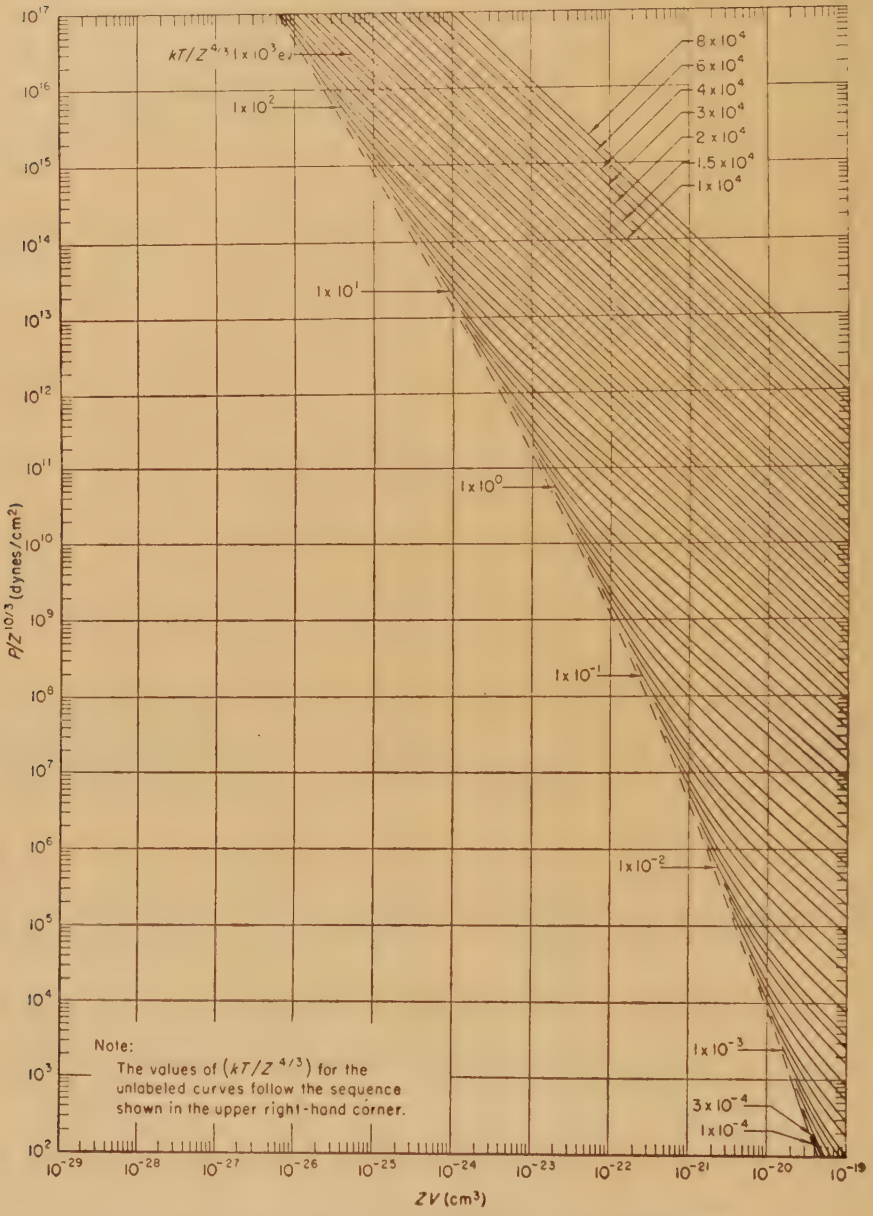
$$\nabla^2V=\frac{16\pi^2e}{h^3}(2mkT)^{3/2}I_{1/2}\left(\frac{eV}{kT}-\frac{eV_0}{kT}\right) \quad . \quad . \quad . \quad (8.31)$$

to be solved for the potential V. In the sphere approximation we have the boundary conditions

$$\left.\begin{array}{ll} V\rightarrow\frac{Ze}{r} \quad \text{as} \quad r\rightarrow 0 \\ \left(\frac{dV}{dr}\right)_R=0 \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad (8.32)$$

The spherically symmetrical solutions of (8.31) satisfying the boundary conditions (8.32) were first examined by Feynman *et al.* (1949) and recently in great detail by Latter (1955 b). The pressure P may be calculated in the present model either by considering the rate of transfer

Fig. 22



Pressure as function of volume for fixed temperatures. (From Latter 1955 b.)

of momentum between the electrons and the surface of the atomic sphere (Feynman *et al.* 1949) or from the thermodynamic relation

$$P = -\left(\frac{\partial F}{\partial v}\right)_T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8.33)$$

where F is the free energy obtained in § 8.4.1 (Brachman 1951). The result may be written

$$P = \frac{8\pi}{3h^3}(2mkT)^{3/2}(kT)I_{3/2}\left(\frac{eV(R)}{kT} - \frac{eV_0}{kT}\right) \dagger \quad . \quad . \quad (8.34)$$

and once V is known the pressure may thus be obtained as a function of temperature T and volume v. Results obtained by Latter (1955 b) and shown in fig. 22 give the pressure–volume relation for a series of temperatures. Latter also gives detailed results for the other important thermodynamic functions in his paper, but we shall not go into further detail here except to say that this very important investigation makes the accurate predictions of the generalized TF theory available over a very wide range of temperatures and densities.

We might also mention here that other, rather different, applications of the generalized TF theory have also been made ; we cite the work of Keller and Meyerott (1952) on the ionization of gas mixtures in stellar interiors as an interesting example.

8.5. *Generalized TF Method with Exchange*

Some work has been done on the inclusion of exchange in the TF theory for non-zero temperature, although practically all of it has been confined to the case of low temperatures. Yokota (1949) was the first to suggest a generalization of the method to include exchange but in this work the Fermi–Dirac distribution function was used, whereas this is not correct when exchange is introduced, as Yokota himself pointed out. A modified form of the distribution function must therefore be used and more refined calculations have been carried out by Umeda and Tomishima (1953 b) (see also March 1953 a). Limited numerical computations were undertaken by Umeda and Tomishima for Fe but apart from these results, no other numerical values are available. In fact, there are reasons for believing that it may well be better to omit exchange if correlation cannot be included as well, and it is doubtful whether further heavy computational work along these lines is justifiable in the present state of the theory.

The only other attempt to include exchange which has been reported in the literature has been made by Latter (1955 b) who also refers to unpublished work by Ashkin and Cowan. The method he proposes appears to be less well based than that referred to above, though it may perhaps be simpler to apply, especially for high temperatures.

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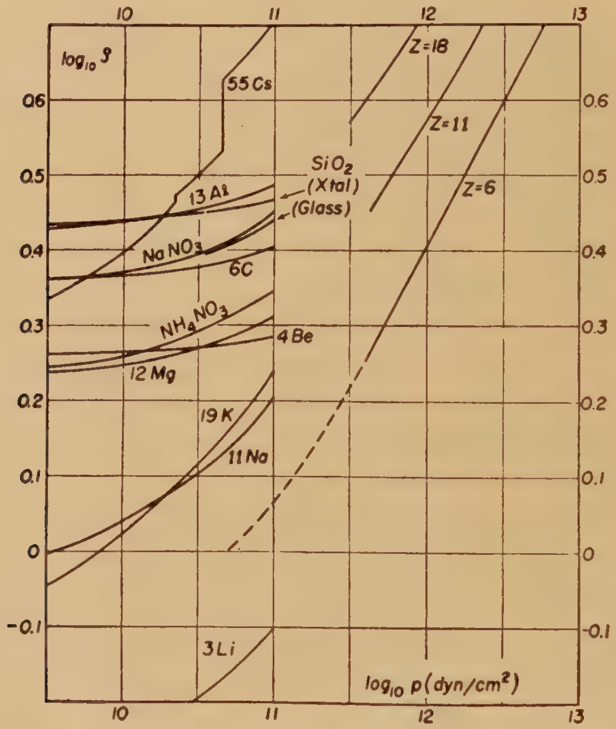
† This expression for the pressure can also be written down immediately from the free electron result using intuitive arguments similar to those given in § 7.1 for the case of zero temperature.

8·6. *Relation of TF Equations of State to Existing Measurements*

As mentioned previously it is possible by means of the techniques devized by Bridgman to reach pressures of 10^5 atmospheres in the laboratory and measurements of this kind now exist for numerous elements and compounds. Most of the results for elements and a few for compounds are shown on the left-hand side of figs. 23, 24 and 25, which have been taken from a paper by Elsasser (1951). These show the relation between the density ρ in g cm^3 and the pressure p in dynes/cm^2†, a double logarithmic plot being used for convenience. On the right of these figures the results obtained from the TFD model for $T=0$ are shown; these were taken mainly from the computations of Feynman *et al.* which have been summarized in fig. 21. It will be seen that the TFD curves have been drawn in figs. 23–25 down to a pressure of about 3×10^5 atmospheres, although, as Feynman *et al.* emphasized, the pressure–density relations derived from the TFD model are likely to be valid only

Fig. 23



Pressure–density relationships.
Curves on left-hand side: experimental results of Bridgman.
Curves on right-hand side: results of TFD theory.
(From Elsasser 1951.)

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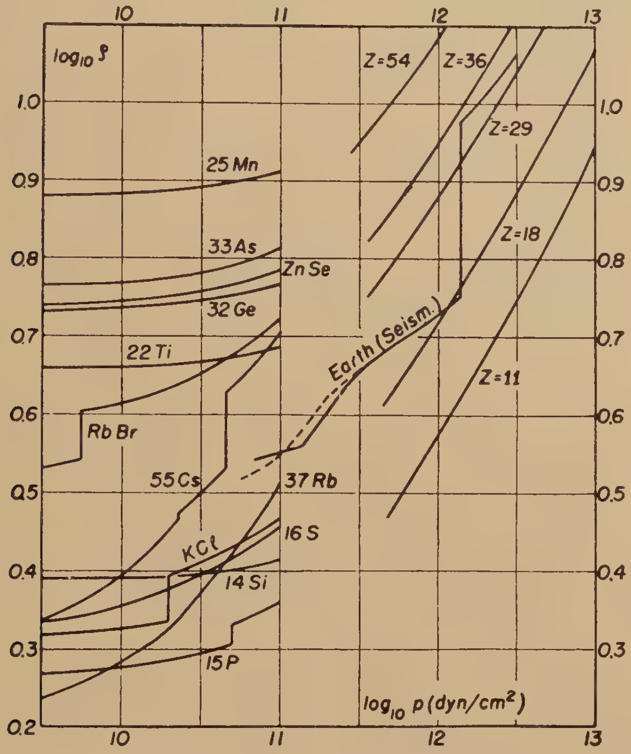
† 10^6 dynes/cm^2 = 0·9869 atmospheres.

for pressures exceeding 10^7 atmospheres†. The theoretical curves in figs. 23–25 show a steady increase of density with increasing atomic number for a given pressure, whereas in Bridgman's results at 10^5 atmospheres such a correlation of density with atomic number is fair, but far from complete.

Fig. 24



Pressure–density relationships.
Curves on left-hand side: experimental results of Bridgman.
Curves on right-hand side : results of TFD theory.
(From Elsasser 1951.)

On the basis of these curves, Elsasser suggested that interpolation between the measured values at low pressures and the computed values at very high pressures should allow densities in the intermediate range to be estimated, with an uncertainty which he suggested should hardly exceed 15–20% anywhere. However, as Bullen (1952) has emphasized particularly, such a suggestion, while interesting, seems unduly optimistic. In fact, it is only necessary to examine a few special cases to see the nature of the difficulties which exist. If we take the case $Z=92$ first, then from fig. 25 the TFD method is found to give a density of $11{\cdot}9$ g/cm^3 at a pressure of $0{\cdot}2\times10^{12}$ dynes/cm^2. This is much lower than the known densities of uranium at pressures from zero to $0{\cdot}1\times10^{12}$ dynes/cm^2. Examination of fig. 25 would seem to indicate that it will not be possible to join the Bridgman curve for uranium smoothly with the TFD curve even at a pressure of approximately 10^7 atmospheres. It may be noted that if we take the case of copper ($Z=29$) as a further example, the density at zero pressure is $8{\cdot}9$ g/cm^3 whereas at a pressure of $1{\cdot}4\times10^{12}$ dynes/cm^2 the value given by the TFD curve shown in fig. 24 is only $8{\cdot}4$ g/cm^3. These examples are sufficient to show that a good deal of caution must be exercized in attempting to predict densities in the range between 10^5 and 10^7 atmospheres, using the TFD curves.

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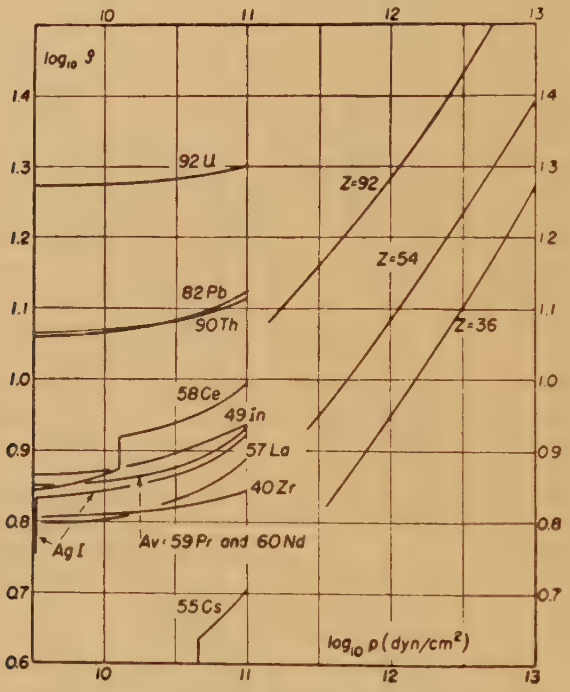
† Elsasser on the other hand suggests a few million atmospheres, beginning at somewhat higher pressures for the light elements and somewhat lower for the heavier elements.

Fig. 25



Pressure–density relationships.
Curves on left-hand side: experimental results of Bridgman.
Curves on right-hand side: results of TFD theory.
(From Elsasser 1951.)

Indeed, a further point should be made here (see particularly Ramsey 1950), namely that it is to be expected that the density of all but the lightest elements will show a series of discontinuous jumps as the pressure increases, corresponding to the breaking down of the inner shells. This will continue until every atom is completely broken down, the electrons then forming an imperfect degenerate Fermi gas. Thus, in this sense, the TFD results, even at extremely high pressures, can at best only be giving an average account of what would seem to be a complicated discontinuous relation between ρ and p for the heavier elements. Of course, when the atoms have been entirely broken down the TFD results should be completely realistic. However the pressures required to bring about this circumstance for the heavier elements are very high indeed. An extremely crude estimate by Ramsey suggests that the critical pressure P for this is

$$P \simeq Z^{5/2} \times 10^{13} \text{ dynes/cm}^2.$$

For the heaviest elements the pressure thus obtained is 10^{12} atmospheres. Pressures a good deal higher than this occur in the interiors of the white dwarf stars, but the maximum pressure in the planets is 3×10^7 atmospheres and this would seem to break down only the lightest elements.

The conclusion to be drawn from this discussion seems to be that even for those lighter elements for which smooth interpolation is possible between the results of Bridgman and the TFD curves (see figs. 23 and 24), the densities thus obtained in the intermediate pressure range should be viewed with reserve. Put another way, it may be that the TFD curves are not physically meaningful until pressures a good deal higher than 10^7 atmospheres are reached.

To obtain more accurate theoretical results than those given by the TFD model is an interesting problem in the theory of solids ; particularly to discuss density changes at phase transitions. In fact, the only substance for which at the moment the equation of state appears to be known with some certainty is solid hydrogen, in the molecular phase up to a pressure of $0 \cdot 8 \times 10^{12}$ dynes/cm², and afterwards in the metallic phase (Wigner and Huntington 1935, Kronig *et al.* 1946, March 1956, see also Ramsey (1950) for a convenient tabulation of the pressure–density relationship). Some work has also been done on helium (Baltensberger ; unpublished calculations reported by Ramsey (1954)) from which it appears that a transition from an insulating to a metallic phase occurs at a pressure of approximately 18 million atmospheres with a density increase from 4·8 to 5·7 g/cm³ †. No other elements have, as yet, been discussed by methods more accurate than the TFD approximation, which of course can give no information of this sort by its very nature ‡.

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† *Note added in proof.*—See also a forthcoming paper by C. A. ten Seldam (1957, *Proc. Phys. Soc.*, in the press).

‡ *Note added in proof.*—It is of interest to note that very recently experimental evidence has been obtained on transitions to metallic states for several ionic and molecular crystals under pressures less than 250 000 atmospheres (Alder, B. J., and Christian, R. H., 1956, *Phys. Rev.*, **104,** 550). Some interesting theoretical work on the phase transition from mixed crystals of ammonia and hydrogen to ammonium metal might also be mentioned (Bernal, M. J. M., and Massey, H. S. W., 1954, *M.N.R. Astro. Soc.*, **114,** 172). Here also the transition pressure is almost certainly less than 250 000 atmospheres.

In spite of deficiencies such as those we have discussed, it may be remarked that the use of the TFD curves shown in figs. 23–25 in conjunction with Bridgman's measurements have enabled a number of interesting conclusions concerning the internal constitution of the earth to be drawn (Elsasser 1951, Bullen 1952). Unfortunately, further discussion along these lines would take us too far from the main theme of this article, and for details we must refer the reader to the original papers.

In concluding this account of the status of the TFD results and their relation to other work, we should draw attention to the fact that shock wave measurements can be used to obtain equations of state of metals in the pressure range between $1{\cdot}5\times10^5$ and 5×10^5 atmospheres (Walsh and Christian 1955). Thus far, results are known only for aluminium, copper and zinc and since they do not essentially affect the discussion already given we shall not go into further details here. Clearly, however, this provides a valuable means of extending the range of pressures over which densities are accessible to experimental measurement. Reference should also be made to some work of Duvall and Zwolinski (1955) who make a comparison between various empirical forms which have been suggested to represent the equations of state of solids and the experimental results of Bridgman and Walsh and Christian, supplemented by the TFD results of Feynman *et al.*; and to an extension of the TF method to deal with compounds (Knopoff and Uffen 1954) †.

§ 9. EXTENSIONS OF THE TF THEORY AND ITS FUNDAMENTAL BASIS

So far we have dealt exclusively with the TF and TFD models. However, various workers have suggested extensions of the TF theory and we shall refer to the most interesting of these quite briefly here. In general it seems fair to say that no method has yet been proposed which can be relied upon to lead to an improvement over the unmodified TF scheme. We shall concentrate mainly on examples which enable a critical assessment of the merits of the various methods to be made.

9.1. *The Extended TF Methods of Weizsäcker and Plaskett*

Two interesting attempts to devise a method which will lead to densities of higher accuracy than those of the original TF theory have been made by Weizsäcker (1935) and Plaskett (1953). We shall deal first of all with these methods in one dimension, assuming that we are discussing the motion of particles in a given potential $V(x)$.

Weizsäcker's method then leads to a second-order differential equation for the particle density ρ, which may be written

$$\frac{h^2}{8m}\rho^2+V-\frac{h^2}{4m}\frac{\rho''}{\rho}+\frac{h^2}{8m}\frac{\rho'^2}{\rho^2}=E' \quad . \quad . \quad . \quad . \quad (9.1)$$

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† *Note added in proof.*—A calculation of the equation of state of water using the TF and TFD models in conjunction with the 'smoothing approximation' (see § 6.2) has just been reported (Latter, A., and Latter, R., 1956, *J. Chem. Phys.*, **25**, 1016).

where E' is to be chosen to satisfy normalization requirements. We shall not go into the details of the derivation of (9.1) (see, for example, Gombás 1949, Berg and Wilets 1955), except to say that whereas the original TF treatment is based on the approximation that the wave functions may be replaced locally by plane waves, Weizsäcker introduced an explicit account of the deviation from plane waves. Several workers have pointed out, however, that Weizsäcker's proof is not really satisfactory (Huang and Wyllie 1949, Berg and Wilets 1955, Swiatecki 1955), and no firm foundation for the method seems to exist. Nevertheless it would appear that the Weizsäcker correction can at least lead to solutions for ρ with qualitatively correct behaviour in that it prevents rapid density variation in regions of rapidly varying potential. Hitherto various workers have used the Weizsäcker term in atomic and nuclear problems, but only recently has any critical examination of the method been made (Ballinger and March 1954, Berg and Wilets 1955) and we shall confine our attention mainly to these investigations.

It is convenient to discuss the results of the Weizsäcker method together with an interesting proposal put forward recently by Plaskett (1953). Plaskett's method, which we shall now outline, is based on an entirely different argument from that of Weizsäcker. Starting from the one-dimensional Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}=(E-V)\psi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9.2)$$

an approximate expression is required for the sum of the squares of the wave functions of, say, the lowest N levels. If the normalized wave functions are denoted by ψ_n, with corresponding energies E_n, then for singly occupied levels the particle density ρ may be written

$$\rho=\sum_1^N \psi_n{}^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9.3)$$

Following Young (1931), Plaskett writes the solution of (9.2) in the form

$$\psi=P^{-1/2}\sin\{\hbar^{-1}\int^x P\,dx+\gamma\} \quad . \quad . \quad . \quad . \quad . \quad (9.4)$$

where γ is an arbitrary constant and $P(x, E)$ satisfies the differential equation

$$\frac{P^2}{2m}-(E-V)-\frac{\hbar^2}{2m}P^{1/2}\frac{d^2}{dx^2}(P^{-1/2})=0. \quad . \quad . \quad . \quad (9.5)$$

The solution which vanishes at $\pm\infty$ must be

$$P^{-1/2}\sin\left\{\hbar^{-1}\int_{-\infty}^{x}P\,dx\right\}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (9.6)$$

where

$$\hbar^{-1}\int_{-\infty}^{\infty}P\,dx=n\pi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9.7)$$

is the equation determining the eigenvalues E_n. This latter expression has, in fact, been used by Milne (1930) as the basis of a practical method for the calculation of eigenvalues, and is, of course, exact. It can now be shown that if a and b are nodes of ψ then

$$\int_a^b \psi^2 dx = \frac{1}{2m}\int_a^b \frac{\partial P}{\partial E}\,dx, \quad \text{. . . . . . . (9.8)}$$

and on the basis of this equation, Plaskett relates $\partial P/\partial E$ to the average density of a single particle (see, however, Berg and Wilets 1955). Using this relation, the sum over the eigenvalues is then replaced by an integration, and an approximation to the density is found after some calculation to be given by

$$\rho=(2/h)P(E_N) \quad \text{. . . . . (9.9)}$$

where E_N is the maximum occupied energy level. It will be seen that (9.7) then ensures that the normalization condition

$$\int_{-\infty}^{\infty} \rho\,dx = N \quad \text{. . . . . (9.10)}$$

is obeyed. Equations (9.5) and (9.9) lead to the differential equation

$$\frac{h^2}{8m}\rho^2 + V + \frac{\hbar^2}{4m}\frac{\rho''}{\rho} - \frac{3\hbar^2}{8m}\frac{\rho'^2}{\rho^2} = E_N \quad \text{. . . . (9.11)}$$

to be solved for the density. This appears superficially to be of a very similar form to Weizsäcker's eqn. (9.1) but, as we shall see, the types of solution are quite different.

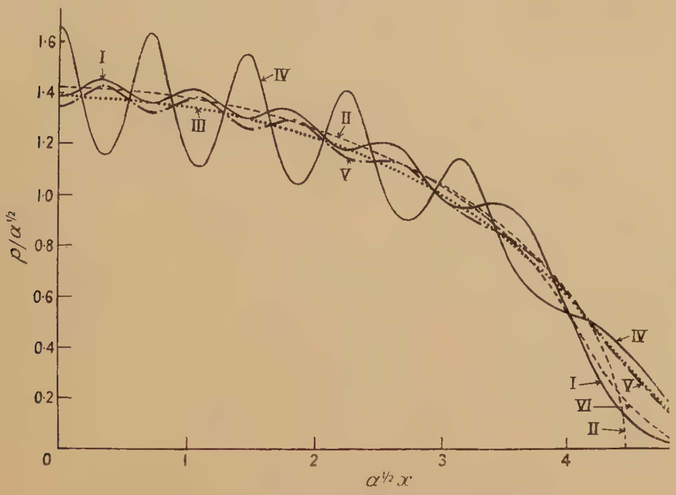
9.1.1. *Densities for the linear harmonic oscillator*

In order to make a critical assessment of the merits of the methods based on (9.1) and (9.11), Ballinger and March (1954) considered the case of a linear harmonic oscillator potential, given by

$$V(x)=2\pi^2 m\nu_0{}^2 x^2 \quad \text{. . . . . (9.12)}$$

where ν_0 is the classical frequency of the oscillator, and their findings are summarized in fig. 26. Curve I shows the exact wave-mechanical density ρ for the first ten levels singly occupied. (For convenience the variables used in fig. 26 are $\rho/\alpha^{1/2}$ and $\alpha^{1/2}x$ where $\alpha=4\pi^2 m\nu_0/h$.) In curve II the results of the original TF approximation have been plotted for comparison, and it can be seen that this provides a good average description of the density, although, of course, the TF curve shows no oscillations and cuts off at a finite distance from the origin. Curve VI shows the density obtained by solving Weizsäcker's eqn. (9.1); the resulting curve is indistinguishable from the TF curve II out to $\alpha^{1/2}x \sim 3$ and the method is evidently not capable of following the fluctuations in the exact wave-mechanical density. However, it will be seen that the behaviour of ρ near the boundary of the classically allowed region, and in the forbidden region, is given more realistically by this method than by the unmodified TF approximation, although the Weizsäcker solution over-estimates the density in the forbidden region.

Fig. 26



Densities for linear harmonic oscillator.
Curve I. Wave-mechanical. Curve II. TF. Curves III–V. Plaskett.
Curve VI. Weizsäcker.
(From Ballinger and March 1954.)

Detailed examination of Plaskett's eqn. (9.11) shows, however, that it does not have a unique solution. Nevertheless it is of interest to note the kind of results to which the method can lead in principle, and three possible densities are shown in curves III–V of fig. 26. It will be seen that III has no oscillations, IV is rather violently oscillatory, while V shows a remarkable degree of correlation with the wave-mechanical density. Unfortunately, as we have already pointed out, there is at present no method of selecting one solution rather than another. It is worth noting finally that all three solutions of Plaskett's equation shown in fig. 26 considerably over-estimate the density in the classically forbidden region and none is even as good as the Weizsäcker density.

9.1.2. *Energies in Weizsäcker's approximation for the three-dimensional isotropic harmonic oscillator*

Following the work on the linear harmonic oscillator discussed above, a further investigation of Weizsäcker's method has been reported by Berg and Wilets (1955). They treat the case of the three-dimensional isotropic harmonic oscillator, with potential

$$V=\tfrac{1}{2}m\omega^2r^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9.13)$$

and discuss the energy in Weizsäcker's approximation. The exact energy levels for the potential (9.13) are given by

$$E_{n_1 n_2 n_3}=(n_1+n_2+n_3+\tfrac{3}{2})\hbar\omega, \quad . \quad . \quad . \quad . \quad . \quad . \quad (9.14)$$

and the number of particles which doubly fill all the energy levels up to and including the levels having major quantum number $N=n_1+n_2+n_3$, is

$$\mathcal{N}=\tfrac{1}{3}(N+1)(N+2)(N+3). \quad . \quad . \quad . \quad . \quad . \quad . \quad (9.15)$$

The corresponding exact total energy is

$$\mathrm{E}_{\mathcal{N}}=\tfrac{1}{8}(N+1)(N+2)^2(N+3)\hbar\omega=\tfrac{3}{4}\mathcal{N}\left[(3\mathcal{N})^{1/3}+\frac{1}{3(3\mathcal{N})^{1/3}}+\ldots\right]\hbar\omega \quad . \quad . \quad . \quad (9.16)$$

whereas the TF energy is

$$\mathrm{E}_{\mathcal{N},\,\mathrm{TF}}=\tfrac{3}{4}\mathcal{N}(3\mathcal{N})^{1/3}\hbar\omega. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9.17)$$

Solving Weizsäcker's equation, which in this case may be written

$$\tfrac{5}{3}\,c_k\rho^{2/3}+c_W\left[\left(\frac{\text{grad}\,\rho}{\rho}\right)^2-\frac{2\nabla^2\rho}{\rho}\right]+V=E' \quad . \quad . \quad . \quad (9.18)$$

where

$$c_k=\frac{3h^2}{10m}\left(\frac{3}{8\pi}\right)^{2/3} \qquad \text{and} \qquad c_W=\hbar^2/8m,$$

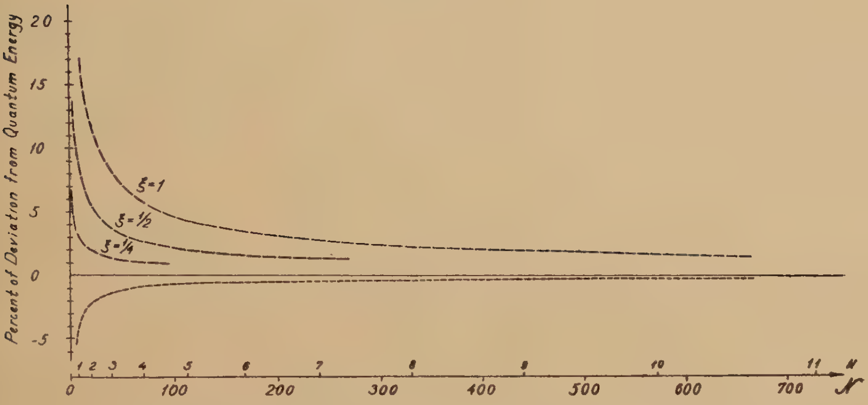
the total energy in this approximation was calculated and the results are represented in fig. 27. The curve marked $\xi=1$ represents the Weizsäcker results, and it will be seen that the errors in the energy are much greater than for the ordinary TF case (lowest curve). The other curves have been obtained by Berg and Wilets by replacing c_W in (9.18) by ξc_W, and it appears from their work that a value of ξ of $\frac{1}{8}$ or less would be necessary to give a substantial improvement over the TF solutions. Such a reduction in the magnitude of the Weizsäcker term has, of course, no theoretical basis. Berg and Wilets also discuss the Weizsäcker solutions for a step potential, but we shall not go into the details of this work here.

The rather dismal conclusion from these investigations is that Weizsäcker's method seems unreliable for use in energy calculations, although it appears to lead to some improvement in the density in the forbidden region.

9.1.3. *Other work on Weizsäcker's method*

The conclusion drawn above is of course based on the examples so far considered and it may perhaps be that for a Coulomb potential, with or without screening, better results would be obtained. In fact, from the early work of Sokolov (1938) and later investigations by Gombás (1953 a, b) this seems rather likely. The latter author has also modified the Weizsäcker method in the case of a small number of particles and has calculated atomic binding energies. There is certainly an impressive improvement in the results compared with the unmodified TF case, but in view of the uncertainty of the validity of Weizsäcker's method as shown by the above discussion, coupled with the absence of a good proof of the basic equations, the discussion of atomic binding energies given in § 5.1 (see also the remarks in § 9.4.3) seems more fundamental. Finally reference should also be made to a variational calculation by Kołos (1956) for the N_2 molecule using Weizsäcker's method.

Fig. 27



Energies for three-dimensional isotropic harmonic oscillator.
The percentage deviation of the TF (lowest curve) and Weizsäcker ($\xi=1$) energies from the quantum-mechanical energies is shown as a function of the number of particles (two per state). Other curves show energies obtained when coefficient c_W is replaced by ξc_W. The major quantum number N is also given on another scale along the abscissa.
(From Berg and Wilets 1955.)

9.2. *Swiatecki's Method*

Swiatecki (1955) has proposed a method by means of which the presence of potential gradients may be taken into account and which may be used in regions of negative kinetic energy. This appears to be quite different from either Weizsäcker's or Plaskett's method, though the aim is the same; namely to obtain more accurate densities than are given by the TF approximation when the potential is varying rapidly. The essential idea behind Swiatecki's work may be stated in the following way. When the TF relation (2.3) is used in any problem with a given potential, the true density is being approximated by the value it would have if the potential were everywhere constant and equal to the actual potential at the point in question. Swiatecki's proposal is to generalize this by approximating to the true density by the value it would have if the potential were everywhere linear, with a slope which is the same as that of the actual potential at the point in question.

Thus the problem reduces to solving Schrödinger's equation for a linear potential and then squaring and adding the normalized wave functions to obtain the total density. The details of this calculation are too involved to go into here, but the final result for the density may be written

$$\rho = 3^{1/2}(4\pi)^{-2} l^{-3} \phi(\xi)\dagger \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9.19)$$

where

$$l^{3} = (8m/9)|V'|/\hbar^2$$

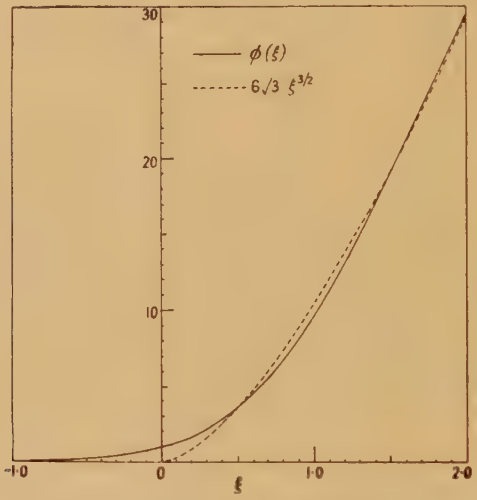
and

$$\xi = (E_0 - V)/l|V'|.$$

Here E_0 is to be determined by normalization requirements, V' is the gradient of the potential and $\phi(\xi)$ is the function shown in fig. 28. For large ξ,

$$\phi(\xi) \doteqdot 6\sqrt{3}\xi^{3/2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9.20)$$

Fig. 28



ϕ in eqn. (9.19) as a function of ξ.
(From Swiatecki 1955.)

and substituting this into (9.19), the original TF relation is regained. Since ϕ is non-zero even when ξ is negative, this method leads to a finite density in regions of negative kinetic energy.

Combining (9.19) with Poisson's equation, a modified TF equation can easily be obtained, and from this Swiatecki shows that at large distances from the nucleus of the atom the density varies as

$$r^{-2} \exp(-r/a)$$

where a is independent of Z. This appears to be some improvement over the r^{-6} dependence of the unmodified TF method. Swiatecki

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† ξ as used here should not be confused with ξ of § 9.1.2.

quotes some unpublished work by Radcliffe in which the modified TF equation has been solved for an atom with $Z=60$. The results of this work are said to show that the corrections to the usual TF densities are not more than a few percent out to quite large radii.

However, it does not seem to have been pointed out that for a potential which is singular as r^{-1} at the origin, Swiatecki's method leads to a density which has a higher order singularity at the origin than the TF density and behaves in fact as r^{-2}. This is discouraging, for it is well known that the chief reason why the TF method is leading to energies which are much too low is because the density near the nucleus is over-estimated. This defect is evidently exaggerated rather than removed by the modified method of Swiatecki, and whilst the method may be useful in other problems, particularly nuclear applications, it is unlikely that it will lead to good results for atoms and molecules.

9.3. *The Density Matrix*

9.3.1. *Comparison of statistical and Hartree–Fock density matrices*

We shall consider now investigations which were designed to throw light on the nature of the approximations involved in the statistical theory rather than to specifically give improved densities. In one such investigation, Fröman (1952) has computed the density matrix for Rb^+, although his analysis is in fact applicable to any atom or ion with closed shells.

Neglecting spin, the density matrix $(\mathbf{r}_0|\rho|\mathbf{r})$ is defined by

$$(\mathbf{r}_0|\rho|\mathbf{r})=\sum_{i=1}^{N}\psi_i^*(\mathbf{r}_0)\psi_i(\mathbf{r}) \quad . \quad . \quad . \quad . \quad . \quad . \quad (9.21)$$

where $\psi_1, \psi_2 \ldots \psi_N$ are the one-electron wave functions of the atom or ion (without the spin factors).

As we have seen, the TF theory can be based on the assumption that over small regions of space the wave functions can be replaced by plane waves. In this case the density matrix is given by

$$(\mathbf{r}_0|\rho|\mathbf{r})=\frac{1}{h^3}\int \exp\left\{\frac{-i\mathbf{p}\,.\,\mathbf{r}_0}{\hbar}\right\}\exp\left\{\frac{i\mathbf{p}\,.\,\mathbf{r}}{\hbar}\right\}d\mathbf{p} \quad . \quad . \quad (9.22)$$

where $d\mathbf{p}$ is the volume element in momentum space. Here the points $\mathbf{r}_0$ and $\mathbf{r}$ should lie close together and around one of the points, say $\mathbf{r}_0$, the allowed range of momenta is from 0 to $p_0(\mathbf{r}_0)$, $p_0(\mathbf{r}_0)$ being determined by the density n at $\mathbf{r}_0$ through eqn. (2.1).

The integral can be easily evaluated by introducing spherical polar coordinates p, Θ, Φ such that Θ is chosen to be the angle between the vectors $\mathbf{p}$ and $\mathbf{r}-\mathbf{r}_0$. Integrating over Θ and Φ leads immediately to the result

$$(\mathbf{r}_0|\rho|\mathbf{r})=\frac{2}{h^2|\mathbf{r}-\mathbf{r}_0|}\int_0^{p_0(\mathbf{r}_0)}\sin\left\{\frac{p}{\hbar}|\mathbf{r}-\mathbf{r}_0|\right\}p\,dp$$

and, hence, performing the integration over p we have

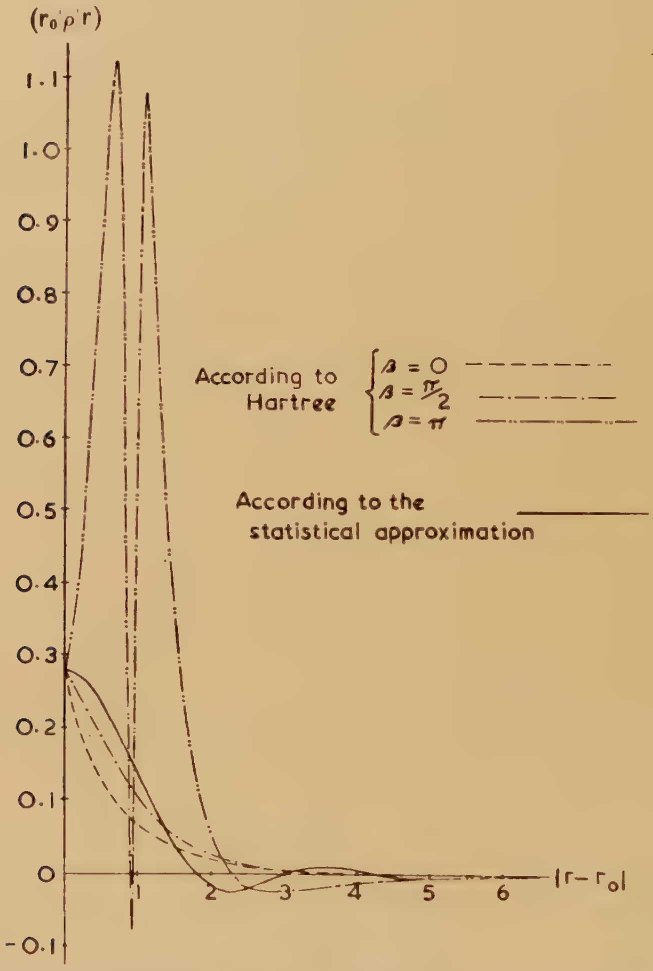
$$(\mathbf{r}_0|\rho|\mathbf{r})=\tfrac{1}{2}n(\mathbf{r}_0)3[\sin\zeta-\zeta\cos\zeta]/\zeta^3 \quad . \quad . \quad . \quad . \quad (9.23)$$

where

$$\zeta=\{3\pi^2 n(\mathbf{r}_0)\}^{1/3}|\mathbf{r}-\mathbf{r}_0|.$$

It can be seen from (9.23) that in the statistical approximation the density matrix depends only on $\mathbf{r}_0$ and $|\mathbf{r}-\mathbf{r}_0|$. Two points should be mentioned in connection with the expression (9.23). Firstly, as we have remarked, the points $\mathbf{r}_0$ and $\mathbf{r}$ should be close together and we should therefore use this expression only for small $|\mathbf{r}-\mathbf{r}_0|$. The justification for using it for all $|\mathbf{r}-\mathbf{r}_0|$ is that both this and the correct density matrix tend to zero rapidly as $|\mathbf{r}-\mathbf{r}_0|$ increases. Secondly, it is usual to take in (9.23) some undefined average of $n(\mathbf{r}_0)$ and $n(\mathbf{r})$.

Fig. 29



Comparison of statistical and Hartree–Fock density matrices for Rb⁺.
($r_0=1$ atomic unit.)
(From Fröman 1952.)

The statistical density matrix (9.23) will now be compared with that given by the Hartree–Fock method. In this case, we can write

$$\psi_i(\mathbf{r})=\frac{f_{nl}(r)}{r}\,Y_{lm}(\theta,\phi) \quad . \quad . \quad . \quad . \quad . \quad . \quad (9.24)$$

where $Y_{lm}(\theta, \phi)$ are the normalized surface harmonics and r, θ, ϕ are the spherical polar coordinates of $\mathbf{r}$. Thus

$$\begin{aligned}(\mathbf{r}_0|\rho|\mathbf{r})&=\sum_n\sum_{l=o}^{n-1}\sum_{m=-l}^{m=l}\left\{\frac{f_{nl}(r_0)}{r_0}\,Y_{lm}(\theta_0,\phi_0)\right\}^*\left\{\frac{f_{nl}(r)}{r}\,Y_{lm}(\theta,\phi)\right\}\\&=\sum_n\sum_{l=o}^{n-1}\frac{f_{nl}(r_0)}{r_0}\frac{f_{nl}(r)}{r}\frac{2l+1}{4\pi}P_l(\cos\alpha) \quad . \quad . \quad . \quad . \quad . \quad (9.25)\end{aligned}$$

by making use of the addition theorem for surface harmonics. Here α is the angle between the vectors $\mathbf{r}_0$ and $\mathbf{r}$.

We can regard this density matrix as a function of r_0, $\mathbf{r}-\mathbf{r}_0$ and β, where β is the angle between $\mathbf{r}_0$ and $(\mathbf{r}-\mathbf{r}_0)$. In order to illustrate explicitly the relation between (9.23) and (9.25), Fröman has made a numerical comparison for the case of the Rb^+ ion, and his results are displayed in figs. 29 and 30. As he points out, even if n were replaced by some average electron density for the points $\mathbf{r}_0$ and $\mathbf{r}$ it would not be possible to remove all deviations between the statistical approximation and the Hartree–Fock density matrix.

9.3.2. *Foundations of the TF theory and the density matrix*

An interesting investigation of the foundations of the TF theory using the density matrix has been reported by Theis (1955 b). This is, essentially, a generalization of the approach of Dirac (1930) in his original paper on the basis of the TF approximation. Dirac's work has been described fully elsewhere (Gombás 1949, Corson 1951) and in view of the fact that Corson's book contains a thorough account of the necessary background to Theis' work, it would not seem profitable to go into the details further here. However, the possibility that the formulation of Theis could be made the basis of a practically useful generalization of the TF theory should certainly be borne in mind, and further work along these lines would seem very worthwhile.

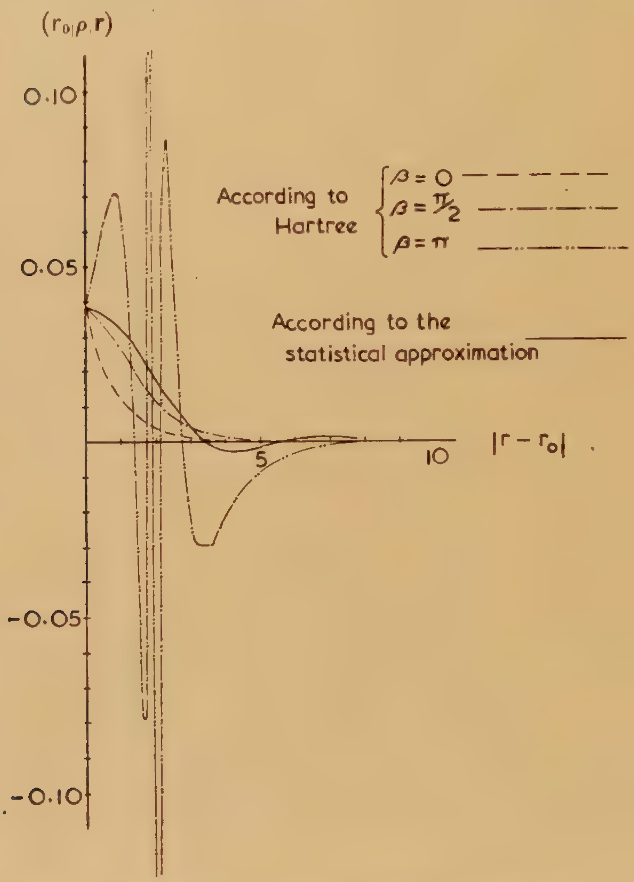
9.4. *Theory of the TF Energy Formula*

Most of the preceding considerations have been concerned with the TF density and with methods of improving this. Here we shall be solely concerned with the energy in the TF theory. We shall see below that a fairly clearcut demonstration of the approximations underlying the usual TF formula for the sum of the eigenvalues can be given. The argument presented is due to March and Plaskett (1956), and demonstrates clearly an intimate connection between the TF theory and the WKB approximation. Of course, it has long been known that such a connection exists, and the accounts of the theory given by Brillouin (1934 a) and Fényes (1949) are both based on the WKB method.

9.4.1. *Sum of the eigenvalues in one-dimensional problems*

As the starting point the usual WKB formula for the eigenvalues in a potential $V(x)$ represented schematically in fig. 31 is adopted. In this

Fig. 30



Comparison of statistical and Hartree–Fock density matrices for Rb⁺.
($r_0=2$ atomic units.)
(From Fröman 1952.)

approximation the eigenvalues are given by the solutions of the equation

$$2\int_{x_1(E)}^{x_2(E)} p(E,x)dx=(n+\tfrac{1}{2})h \qquad (n=0,1,2\ldots) \quad . \quad . \quad (9.26)$$

where $p(E,x)=\{2m(E-V)\}^{1/2}$, and x_1 and x_2 are the classical turning points given by the solutions of

$$V(x)=E. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9.27)$$

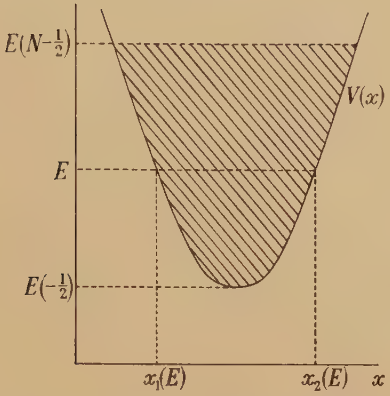
It is now convenient to regard n as a continuous variable, which is the function of E defined by (9.26). The eigenvalues are then given by

$$n(E_0)=0, \quad n(E_1)=1, \ldots n(E_k)=k, \ldots, \qquad (9.28)$$

and we wish to calculate the sum of the first N eigenvalues, say E, given by

$$\mathrm{E}=\sum_{k=0}^{N-1} E_k. \qquad (9.29)$$

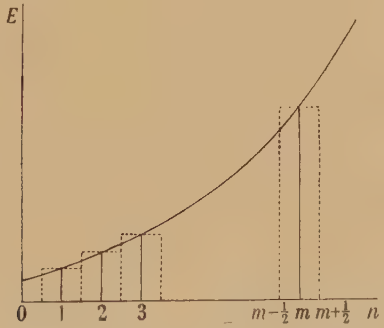
Fig. 31



(E, x) plane for one-dimensional case.
(From March and Plaskett 1956.)

In fig. 32, a possible form of $E(n)$ is shown ; from this we can find the eigenvalues from the ordinates corresponding to integral values of n and summing we obtain E. From a geometrical point of view, this is equivalent to summing the areas of the rectangles shown in fig. 32. This

Fig. 32



$E(n)$ represented schematically.
(From March and Plaskett 1956.)

suggests immediately that it will often be quite an accurate approximation to replace the area of each rectangle, say the one centred on $n=m$, by the area enclosed between the curve $E=E(n)$ and the ordinates $n=m-\frac{1}{2}$ and $m+\frac{1}{2}$. The approximation to the sum E thus obtained is

$$\mathrm{E}=\int_{-1/2}^{N-1/2} E(n)dn \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9.30)$$

where the limits of integration are obviously to be chosen as shown. In passing, it is worth noting that no approximation is involved in writing (9.30) if the function $E(n)$ is linear.

The expression (9.30) is now easily simplified by changing the variable of integration to E, using (9.26). The result is

$$\mathrm{E}=\int_{E(-1/2)}^{E(N-1/2)}\int_{x_1(E)}^{x_2(E)}\frac{2m}{h}Ep^{-1}(E,x)dxdE. \quad . \quad . \quad . \quad (9.31)$$

Changing the order of integration and noting that the integration is over the shaded portion of the (E, x) plane shown in fig. 31 we have

$$\mathrm{E}=\frac{2m}{h}\int_{x_1(E')}^{x_2(E')}\int_{E=V(x)}^{E'} Ep^{-1}(E,x)dEdx \quad . \quad . \quad . \quad . \quad (9.32)$$

where $E(N-\frac{1}{2})$ has been replaced by E' for convenience. The integration over E can now be performed and it is then easily shown that

$$\mathrm{E}=\int_{x_1(E')}^{x_2(E')}\left[\frac{1}{3}\frac{p^2(E',x)}{2m}+V(x)\right]\frac{2}{h}p(E',x)dx \quad . \quad . \quad (9.33)$$

where E' is determined by

$$\int_{x_1(E')}^{x_2(E')}\frac{2}{h}p(E',x)dx=N. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9.34)$$

This is the usual TF formula for the sum of the eigenvalues in a one-dimensional problem; in the TF scheme the quantity $(2/h)p(E',x)$ is further identified with the particle density.

The conclusion from this argument is that the TF energy is given exactly by (9.30), where $E(n)$ is determined by the WKB formula (9.26). Or put another way, two approximations are involved in using the TF formula for the sum of the eigenvalues in any one-dimensional problem with a given potential $V(x)$. The first is to start from the WKB formula for the individual eigenvalues, and the second is to replace the summation over these by an integration. As March and Plaskett (1956) have discussed in some detail, the second approximation may in some cases be corrected by adding some terms in the Euler–Maclaurin summation formula, but we shall not go into details here. It seems much more difficult to make any correction for the use of the WKB formula, but Langer (1949) has established that (9.26) has approximate validity down to low values of n for a fairly wide range of potentials, and this is therefore usually the less serious of the two approximations. One attractive method which immediately suggests itself is to use expression (9.7) for the eigenvalues instead of (9.26) but so far it has not proved possible to make progress along these lines.

9.4.2. *Three-dimensional case with spherical symmetry*

Of more practical importance than the one-dimensional case discussed above is the sum of the eigenvalues for a central field problem, with potential $V(r)$. In this case the WKB approximation to the eigenvalue E_{kl} is given by the solution of the equation

$$2\int_{r_1^l(E)}^{r_2^l(E)}\left\{2m\left[E-V(r)-\frac{\hbar^2}{2m}\frac{(l+\frac{1}{2})^2}{r^2}\right]\right\}^{1/2}dr=(k+\tfrac{1}{2})h, \quad . \quad (9.35)$$

where $r_1^l(E)$ and $r_2^l(E)$ are the roots of the equation

$$V(r)+\frac{\hbar^2}{2m}\frac{(l+\frac{1}{2})^2}{r^2}=E. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9.36)$$

Here k is not the total quantum number ; this is $k+l+1$ and $(l+\frac{1}{2})^2$ has been written in (9.35) instead of $l(l+1)$ for the reasons discussed by Langer (1937).

We shall not give the argument in detail for this case as it follows entirely the same lines as that used above for one-dimensional problems, although (see below) it does contain an additional approximation. The sum of the eigenvalues now required is

$$\mathrm{E}=\sum_{k,\,l\ \mathit{integers}\geqslant 0}(2l+1)E(k,l) \quad . \quad . \quad . \quad . \quad . \quad . \quad (9.37)$$

for all k, l satisfying the condition $E(k,l)\leqslant E''$ say, where E'' is determined by the number of levels considered in any given problem. The usual TF expression for this sum can then be shown to be entirely equivalent to the approximation

$$\mathrm{E}\doteqdot\iint(2l+1)E(k,l)dkdl, \quad . \quad . \quad . \quad . \quad . \quad . \quad (9.38)$$

where the number of states over which the summation in (9.37) is to be extended is replaced by an integral, namely

$$\sum_{k,l}(2l+1)\doteqdot\iint(2l+1)dkdl. \quad . \quad . \quad . \quad . \quad . \quad . \quad (9.39)$$

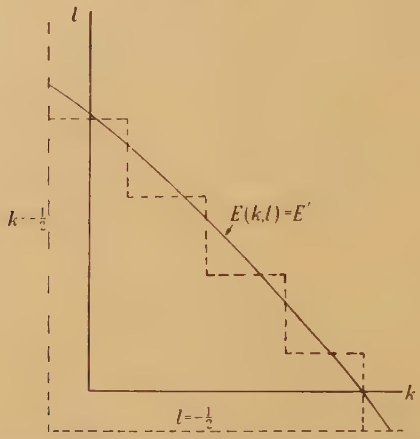
The region of integration in both (9.38) and (9.39) is to be taken as that bounded by

$$k=-\tfrac{1}{2}, \qquad l=-\tfrac{1}{2} \qquad \text{and} \qquad E(k,l)=E' \quad . \quad . \quad . \quad (9.40)$$

where E' is to be chosen so that the integral in (9.39) is equal to the total number of occupied states. Unlike the one-dimensional case, however, two approximations are involved in passing from (9.37) to (9.38) ; in addition to the replacement of the sum by an integral, the region of integration defined by (9.40) is not correct. Instead of the curve $E(k,l)=E'$, the boundary should be composed only of lines corresponding to values of k and l equal to half odd integers, as shown in fig. 33.

Using this formulation, a thorough and instructive analysis of the errors in the Coulomb field case can be made. This is relevant to the calculation of atomic binding energies, and for the details, reference should be made to the discussion of March and Plaskett.

Fig. 33



(k, l) plane illustrating regions of integration in central field problem. (From March and Plaskett 1956.)

9.4.3. *Errors in the TF sum of eigenvalues for the screened potential of the TF theory for atoms*

Besides allowing a detailed examination of the errors introduced by the use of the TF approximation in the Coulomb field case to be made, the above discussion also suggests a method for estimating the errors made when the TF expression for the sum of the eigenvalues is used for the proper screened potential of the TF theory for isolated atoms, on which the theory of atomic binding energies given in § 5.1 was based. The TF sum can be obtained from the energy (5.6), by correcting for the well known fact that the sum of the eigenvalues includes twice the mutual potential energy of the electronic cloud. This latter energy is easily obtained from known energy relationships in the TF theory, and it turns out that the sum of the eigenvalues is just two-thirds of the total energy (5.6), or

$$-0{\cdot}5125Z^{7/3} \text{ atomic units.} \quad . \quad . \quad . \quad . \quad . \qquad (9.41)$$

Referring back to the discussion of atomic binding energies in § 5.1, we can now regard Scott's work as an attempt to correct for the difference between (9.41) and the WKB sum for the proper TF potential. That this point of view is legitimate is due to the fact that Scott's argument reduced the problem to the Coulomb field case, and it is well known that the WKB formula (9.35) then leads to the exact eigenvalues. By computing the WKB eigenvalues numerically from (9.35) for the proper screened potential of the TF theory for $Z=18$, March and Plaskett made a revised estimate of the correction term of order $Z^{5/3}$ in the formula for the sum of the eigenvalues, and in this way the binding energy formula (5.8) was obtained.

9.4.4. *Macke's derivation of the TF energy expression*

A further and very interesting discussion of the foundations of the TF energy expression and its various generalizations has been given by Macke (1955 a, b) who starts from the Ritz variation method of finding one-electron wave functions in an N-electron problem. If a set of normalized and orthogonal one-electron wave functions is denoted by ψ_n and the total wave function Ψ of the system is taken as a single determinant formed from these one-electron functions, then the best ψ_n's in the sense of the variation method are, of course, to be obtained by solution of the Hartree–Fock equations. However, such a 'best' set of functions is not sought here, but a certain restricted class of trial function is adopted. In the approximation referred to above, with arbitrary ψ_n, the particle density ρ may be written

$$\rho = \sum_{n=1}^{N} |\psi_n|^2 \qquad (9.42)$$

and the kinetic energy T as

$$T = \int \frac{\hbar^2}{2m} \sum_{n=1}^{N} |\text{grad}\, \psi_n|^2 d\tau. \qquad (9.43)$$

The one-electron wave functions $\psi_n(\mathbf{r})$ are now represented by Macke in terms of a known orthogonal system of functions $\phi_n(y_k)$ where y_k represents a transformation of the space :

$$y_k = y_k(\mathbf{r}), \qquad k = 1, 2, 3 \qquad (9.44)$$

the details of which are largely arbitrary but which is taken to transform the whole of space into a box of unit length. The trial wave functions ψ_n are then taken as

$$\psi_n(\mathbf{r}) = (\sigma/N)^{1/2} \phi_n(y_k) \qquad (9.45)$$

where σ/N is defined as the determinant $|\partial y_k/\partial x_\lambda|$. The special choice of ϕ_n made by Macke is the set of normalized eigenfunctions in the box of unit length. With these assumptions for σ and ϕ_n the functions $\psi_n(\mathbf{r})$ are normalized and orthogonal for all y_k.

For one-electron functions of the form (9.45), it is easy to show that the kinetic energy T given by (9.43) can be expressed in the form

$$T = \int \frac{\hbar^2}{2m} \left\{ \frac{\sigma}{N} \sum_{1}^{N} |\text{grad}\, \phi_n|^2 + (\text{grad}\, \sqrt{\rho})^2 - \sigma(\text{grad}\, \{\rho/\sigma\}^{1/2})^2 \right\} d\tau \qquad (9.46)$$

while ρ is evidently given by

$$\rho = \frac{\sigma}{N} \sum_{1}^{N} |\phi_n|^2. \qquad (9.47)$$

Since

$$\frac{1}{N}\sum_{1}^{N}|\phi_n|^2 \to 1 \qquad \text{as} \qquad N \to \infty\dagger,$$

it will be seen that ρ goes over into σ for N very large.

The rest of Macke's argument now depends on the evaluation of the first term of (9.46) in the limit of N large. We shall not go through all the details here, but simply state the result that this then goes over into the usual kinetic energy term of the TF theory, namely

$$c_k\int \rho^{5/3}d\tau \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9.48)$$

where it is permissible to write either ρ or σ in (9.48). Clearly in this approximation the third term in (9.46) is negligible, while the second as it stands is simply the Weizsäcker correction. If the kinetic energy is taken as

$$T=c_k\int \rho^{5/3}d\tau+(\hbar^2/2m)\int(\text{grad}\sqrt{\rho})^2d\tau \quad . \quad . \quad . \quad (9.49)$$

and the potential energy is written in terms of ρ, then minimization of the total energy leads to Weizsäcker's equation in the usual way.

However, the writer feels that such an argument cannot, as it stands, be taken as establishing the Weizsäcker method on a firm basis. For in evaluating the first term in (9.46) the assumption $N \to \infty$ is made, and in this limit the Weizsäcker term can also be dropped as it is negligible compared with the usual TF term (9.48). Or, put another way, in writing (9.49), no attempt has been made to show that terms of the same order of magnitude as the Weizsäcker term have not been omitted from the first term of (9.46). It would certainly be interesting if, for a given potential V say, the Weizsäcker energy could be shown to be always greater than the correct value‡ along the lines of Macke's work. It should also be noted here that besides Macke's claim that the Weizsäcker energy term results from his arguments, he indicates also that corrections of the type discussed by Gombás (1953 a, b) which appear when N is not large, can be obtained by a modification of the method, but no details are given.

In spite of the reservations which, the writer feels, are to be attached to Macke's discussion, at least in its present form, this must be regarded as a promising line of attack on many-body problems in which it might

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† For example, for a one-dimensional box of unit length, $\phi_n(y)=2^{1/2}\sin(n\pi y)$ and

$$\sum_{1}^{N}\phi_n^2=2\sum_{1}^{N}\sin^2(n\pi y)=(N+\tfrac{1}{2})-\frac{\sin[\pi(2N+1)y]}{2\sin(\pi y)}$$

and evidently

$$\frac{1}{N}\sum_{1}^{N}\phi_n^2 \to 1 \qquad \text{as} \qquad N \to \infty.$$

‡ The writer is not aware of any example which has been worked out which violates this, although so few cases are available that this should not be taken as serious evidence from which to infer any general result.

well be possible to make direct use of results which have been worked out in the original TF approximation and also in the Weizsäcker approximation in an iterative scheme based on the treatment outlined here†. Whether such a scheme with the restricted form of trial function (9.45) can lead to results of comparable accuracy to those obtained by the Hartree–Fock method, while still keeping the amount of labour down to a small fraction of that involved in such calculations for many particles, remains to be seen. Macke has already announced detailed applications of his method but as far as the writer is aware, none has been published as yet.

9.5. *Relativistic Generalization of the TF Method*

The treatments discussed so far have all been based on the non-relativistic case, although an approximate relativistic correction to be applied to the binding energies of atoms was given in § 5.1. In concluding this review we shall make brief reference to the modifications caused by inclusion of relativistic effects.

The earliest attempt to formulate a relativistic TF equation (Vallarta and Rosen 1932) was largely unsuccessful, as the resulting charge density could not be normalized. Jensen (1933) proposed that this difficulty be circumvented by taking account of the finite extent of the nucleus, but this can hardly be regarded as a satisfactory solution. Plaskett (1953) derived a relativistic modification of the TF theory based on the Klein–Gordon equation; this avoided normalization difficulties but had various rather unsatisfactory features. However, the most recent work (Gilvarry 1954 a) is based on an expression for the density of states derived by Rudkjøbing (1952) from the Dirac equation for the case of a spherically symmetrical potential and appears to remove the difficulties of previous work, although no practical application has been made as yet.

Rudkjøbing's result for the number of states $n(r, E)$ per unit volume and per unit energy range, may be written

$$n(r, E) = \frac{8\pi}{h^3c^3}\left[(E+eV)^2 - m^2c^4 - \left(re\frac{dV}{dr}\right)^2\right]^{1/2}(E+eV) \qquad (9.50)$$

where V is the electrostatic potential and c is the velocity of light. If E_m is the maximum energy of the electrons, to be determined by normalization requirements, the relativistic TF equation based on (9.50) may be written

$$\begin{aligned}\frac{1}{r}\frac{d^2}{dr^2}(rV) &= \frac{32\pi^2 e}{3h^3}(2m)^{3/2} \\ &\times\left\{E_m - mc^2 + eV + \frac{[(E_m - mc^2 + eV)^2 - (re[dV/dr])^2]}{2mc^2}\right\}^{3/2}. \qquad (9.51)\end{aligned}$$

---

† *Note added in proof.*—Macke's proposals have now been developed rigorously for particles moving in a common one-dimensional potential, and a new variational method formulated for the calculation of particle densities and sums of eigenvalues (March, N. H., 1957, *Proc. Phys. Soc.* A, **70,** 169).

It is easily shown that for a potential Ze/r, the electron density varies as $r^{-3/2}$ as $r \to 0$, and can therefore be normalized. The energy term $[re(dV/dr)]^2$ can be interpreted as due to spin-orbit coupling of the electrons; and if this term is omitted in (9.51) the resulting equation is essentially the same as that derived by Vallarta and Rosen (1932).

As Gilvarry (1954 a) has pointed out, it should be sufficient for most purposes to solve (9.51) by a perturbation procedure, based on the usual non-relativistic TF solution, and the perturbation equation can in fact be solved analytically in terms of this solution. Gilvarry has announced, but not yet published, an investigation to obtain accurate values for the relativistic corrections to be applied to atomic binding energies. The generalization of (9.51) to the case of elevated temperatures has also been given by Gilvarry and an approximate method of including exchange outlined.

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The Experimental Study of the Optical Properties of Metals and the Relation of the Results to the Drude Free Electron Theory

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INTRODUCTION

THIS paper is concerned primarily with the experimental aspects of the subject; for the most part it deals with results obtained with recently developed methods. The only theory considered is the Drude free electron theory which was used as a guide in selecting the most promising experiments and in classifying the results. The anomalous skin effect is treated as an extension of this theory. In addition to determining the range of application of the Drude theory, an effort was made to obtain results of interest to workers in solid state physics. It is hoped that the mode of presentation will make the results of value not only to those in the field but to all who might have an interest in their significance. The contents are arranged as follows: §§ 1–5 are on general considerations—§ 1, absorption of electromagnetic radiation by metals; § 2, the Drude free electron theory; § 3, the anomalous skin effect; § 4, conclusions suggested by older experimental work; and § 5, general features of the approach and of the procedures used in recent experiments. Section 6 describes experimental methods of making measurements, and § 7 presents recent experimental results. Finally, § 8 gives conclusions drawn from the experimental results.

Fig. 1

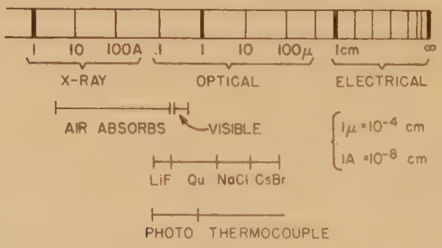


Diagram showing the electromagnetic spectrum with the wavelength limits for the three regions, x-ray, optical, and electrical. Also indicated are the transmission properties of several optical materials.

§ 1. ABSORPTION OF ELECTROMAGNETIC RADIATION BY METALS

A convenient approach to a discussion of the optical properties of metals is to indicate roughly the extent of our knowledge concerning the more general problem of the absorption of electromagnetic radiation by metals. The sketch shown in fig. 1 will aid in making a quick survey. Wavelengths in commonly employed units are given for each of the three regions arbitrarily called x-ray, optical, and electrical.

In the x-ray region the absorption properties of matter are independent of the physical state, that is, x-rays are characteristic of atoms and not of the state of aggregation. The field of x-ray spectroscopy (Seigbahn and Manne 1925, Hirsh 1942) and its relation to atomic structure has been worked out to all but the finest details, and it is now possible to find information in well organized and tabulated form. This situation prevails only for the shorter wavelengths, however. As the wavelength increases to about 100 Å and above, the absorption is associated with the uppermost energy levels of an atom which do depend on the state of aggregation. In this region so called ‘ soft x-rays ’ have been used to investigate the density of these levels (Skinner 1938, Shaw 1956). Early work on alkali metals gave significant results and lead to optimism concerning the possibility of studying other types of metals by the same technique. In spite of improved instrumentation there are still experimental difficulties. These, together with the lack of a satisfactory guiding theory, have led to the disappearance of the early enthusiasm. At the present time the standard x-ray region is bounded by a frontier at the long wavelength side located at roughly a few hundred angstroms.

In the middle of the spectrum of fig. 1, in the more restricted optical region, there was great interest about 1890 to 1915. Drude led the way by developing his free electron theory of metals and also by devising and performing experiments (Drude 1902, Born 1943). There was usually a rough qualitative agreement between theory and experiment and in a few selected cases rather good agreement in certain wavelength regions. In spite of a long period of experimental work, some of it continuing to the present time, no clear cut conclusions have been reached concerning the validity and the limitations of the theory. It is now agreed that for the most part the experimental work has not been reliable because of defects in the samples on which the optical measurements were made.

In the region of very long wavelengths labelled ‘electrical’ in fig. 1, absorption of radiation has been understood almost since the time of Faraday. In fact, the theory of the classical skin effect (Stratton 1941) which describes optical phenomena in this region is now part of electrical engineering technology. It was never really clear however just how far this theory remained valid as the wavelength was shortened. As will be shown later, Hagen and Rubens (1903) went somewhat too far. Also, it must be mentioned that recent experiments in the microwave region of a few centimeters have led to results of great importance to the general problem of absorption of radiation by metals. These results lead to the development of what is now called the ‘ anomalous skin effect ’ ; it will be discussed at the appropriate place later.

Looking at the whole situation as presented in fig. 1 the extremes are best understood : the atomic properties of the x-ray region, and low frequency electricity. The most promising region for future study can be determined only after some attention has been given to existing theories. Also, since any actual experiment is selected only after thought has been given to problems of instrumentation, some practical information has been added to the bottom of fig. 1. The visible region will usually be too limited to give conclusive results. As indicated the ultra-violet below the quartz lower limit is especially difficult to study because of air absorption, and also because of the absence of suitable light sources, detectors, and transmitting materials. The infra-red appears more amenable to experimental investigation at least at the present time.

§ 2. THE DRUDE FREE ELECTRON THEORY OF METALS

The usual procedure for beginning a discussion of the free electron theory of metals is to pay high, but brief, respects to Drude for suggesting the general ideas and then immediately to begin pointing out the inadequacies of his theory. This might indicate that Drude's contribution was hardly more than a starting point toward explaining the nature of metals, and indeed when one considers developments since 1900 this procedure is justifiable. In the field of optics, however, the situation is somewhat different in that Drude's explanation of the optical properties of metals is quantitatively correct in those situations where it applies. The equations given by Drude relate the optical properties to electrical parameters. Since optical phenomena are essentially only high frequency electricity, the equations are rather limited in what they claim to do and therefore have a much greater likelihood of being correct. The free electron theory of Drude will now be examined for the purpose of finding the most promising experiments for testing the theory and providing information for extending it. Actual derivation of the equations will not be included since this can be found in standard texts (Seitz 1941, Mott and Jones 1936).

In an effort to preserve the general approach of the first section a comparison will be made of electromagnetic wave propagation in two types of solids, dielectrics and metals, and for the several wavelength regions of fig. 1. About 1880 Lorentz explained absorption in dielectrics by assuming bound charges which became polarized by the passing light wave (Lorentz 1906). Equation (1) is the usual one for describing such a phenomenon.

$$m\ddot{x}+\gamma\dot{x}+Kx=E\sin\omega t, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

m is the mass of the oscillator, γ is a damping factor, and K is an elastic constant. A theory based on the physical ideas associated with eqn. (1) explained most of the observed optical properties of dielectrics.

The contribution of Drude was to consider the case of free rather than bound charges. Free charges mean that the elastic constant of eqn. (1)

is taken as zero; accordingly the last term on the left drops out leading to eqn. (2);

$$m\ddot{x}+\gamma\dot{x}=E\sin\omega t. \qquad (2)$$

For completeness and to show the relationship of the various theories eqn. (3) for the classical skin effect is included. At low frequencies the enertial reaction of the electron is small relative to the resistive damping, therefore only one term remains on the left:

$$\gamma\dot{x}=E\sin\omega t. \qquad (3)$$

Equation (3) does not require a definite model, in fact any model will do, even the fluid model of Faraday is satisfactory. On the other hand eqn. (2) requires a model, at least to the extent that approximately free conduction electrons are visualized. Other details of the model are not too significant. For example, although the concept of mean free path was used by Drude, his assumption that it was approximately equal to the atomic separation was grossly incorrect.

Starting with eqn. (2) and the model on which it is based, Drude developed the relationship given in eqns. (4) through (6) between optical and electrical properties of a metal.

$$n^2-k^2=1-2\left(\frac{Ne^2}{2\pi m^*}\right)\frac{1}{\nu^2+\gamma^2}, \qquad (4)$$

$$nk=\frac{\gamma}{\nu}\left(\frac{Ne^2}{2\pi m^*}\right)\frac{1}{\nu^2+\gamma^2} \qquad (5)$$

$$\gamma=\left(\frac{Ne^2}{2\pi m^*}\right)\frac{1}{\sigma}. \qquad (6)$$

In these equations n and k are defined through the complex index of refraction $\mathbf{n}=n-ik$; e is the charge of the electron and m^* its effective mass; N is the number of free electrons per unit volume; σ is the d.c. conductivity of the metal; and ν is the frequency of the radiation.

Equations (4) to (6) will be taken to represent the essence of Drude's free electron theory as applied to the optical properties of metals. Zener (1933), in more recent times, revived the theory to account for the observation of Wood (1933) that the transmission of the alkali metals in the ultra-violet is relatively high. Some of the concepts of the theory have been reinterpreted by Kronig (1931, 1933).

Again for completeness the equation for the classical skin effect is included.

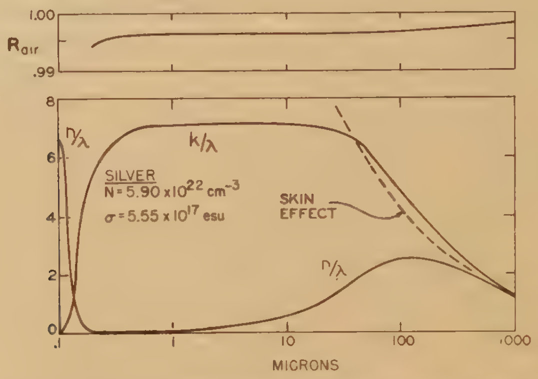
$$n=k=(\sigma\lambda)^{1/2}. \qquad (7)$$

As indicated, n and k are equal and each is proportional to the square root of the conductivity. The electron mass and density do not appear. Equation (7) is the form taken by eqns. (4) and (5) for very long wavelengths.

In using Drude's equations it is common practice to assume that the number of free electrons per atom is equal to the chemical valence, that is, for a monovalent metal such as Ag the electron and atomic densities are equal. Lacking other information, the effective mass is taken equal to the free mass.

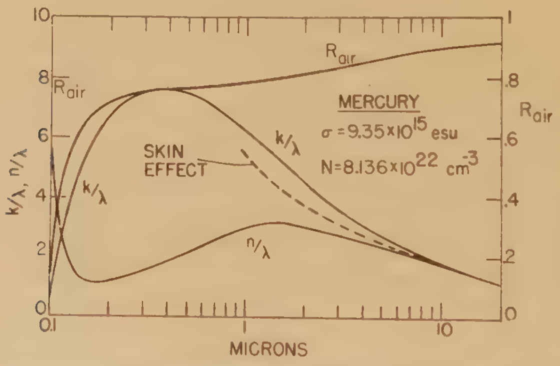
The equations become more meaningful after numerical values are inserted. This has been done for Ag (a very good conductor) and for liquid Hg (a relatively poor conductor). The results are shown in figs. 2 and 3 where k/λ and n/λ are used as the optical parameters because this form makes it more convenient to cover a long wavelength range on a single graph. Also, it is natural to use this form for the transmission experiments which will be described later. Values used in the calculations for N (electrons per cm^3) and for σ (e.s.u.) are shown on the graphs.

Fig. 2



Graphs for Ag showing the wavelength variation of n/λ, k/λ, and the reflectivity R_{air} as found by calculation using the Drude theory. (R_{air} means the reflectivity at normal incidence in air.) Schulz (1954 b).

Fig. 3



Graph for Hg showing the wavelength variation of n/λ, k/λ, and the reflectivity R_{air} as found by calculation using the Drude theory. Schulz (1957 a).

Inspection of fig. 2 for Ag reveals certain features which can serve as guides in the development of experimental procedures. It is only in the very long wavelength region, 500 μ and longer, that n and k become equal and their common value becomes identical with that given by the classical skin effect. This leaves a very long wavelength region of about 0·3 μ to 100 μ in which the predictions of the Drude theory can be explored. In the range of about 1 μ to 10 μ the value of $k \gg n$, a condition which permits rewriting of eqn. (4) in a simplified form :

$$k/\lambda = (Ne^2/\pi m^*)^{1/2}. \qquad (8)$$

If Ag or a similar metal follows the Drude theory, eqn. (8) indicates that a transmission experiment alone will permit an evaluation of the ratio N/m^*. In a rough way one can think of the k/λ curve in fig. 2 as measuring the inertial reaction of the electrons. It is often rather dogmatically stated that since there are two constants n and k to be evaluated one must perform two independent experiments. Figure 2 shows that this is not completely true. Further inspection of the region from 1 μ to 10 μ shows that the quantity n/λ^2 is nearly constant. Since for the wavelength region being considered the reflectivity depends on the quantity n/k^2, it follows that the reflectivity is also nearly a constant. It may appear that the reflectivity is more dependent on k than on n. This is in fact true, but k can usually be determined so much more accurately than n (and by an independent transmission experiment) that experimentally n can be determined by the reflectivity.

Attention to the absolute values on the graph of fig. 2 will help to emphasize some of the experimental difficulties to be overcome. As just pointed out, there is very small dispersion or variation with wavelength. Since there are no absorption edges to measure it is necessary to measure intensities. This requires photometry which is usually a difficult procedure especially for such metals as Ag for which the reflectivity can be 99% or higher. A second type of difficulty arises from the very high value of k/λ. For metals such as Ag the intensity of the radiation in the visible region that gets through the surface drops to 1% in a few hundred angstroms. If transmission experiments are to be done, this means very thin samples and the situation gets worse as the wavelength is increased. Accordingly, whether one uses reflectivity or transmission methods there are difficulties in studying those metals which are good conductors.

Turning now to fig. 3 for Hg and the case of poor conductors in general, it is evident that there are some great differences from Ag. There is no plateau in k/λ, only a maximum which occurs at or near the visible. In addition n/λ is not small and the reflectivity is much lower than for Ag. On the whole then it might be expected that poor conductors are easier to study, but a limitation of a fundamental character arises from the position of the k/λ maximum. There is only a limited working range of about 0·2 μ to 5 μ. If the metal has absorption other than that arising from the conduction electrons, it is possible that there will be no wavelength region in which the Drude theory can be tested. Although other mechanisms of absorption tend to be strongest toward the ultra-violet, their effects often trail off into the near infra-red and sometimes even into the skin effect region.

§ 3. ANOMALOUS SKIN EFFECT

From eqn. (7) for the classical skin effect an expression can be derived for the absorption A, or reflectivity R, of a metal surface at normal incidence :

$$A=(1-R)=2(\nu/\sigma)^{1/2}. \qquad (9)$$

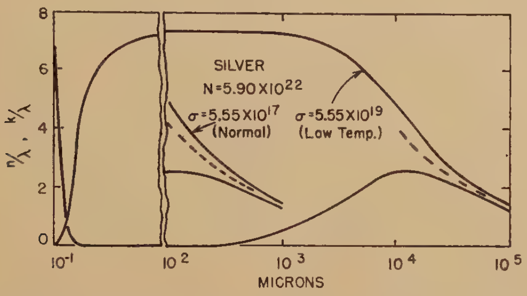
It is clear from eqn. (9) that at low temperatures (where σ is high) all metals should become exceedingly good reflectors, in particular this should be true below the transition temperature of superconductors. Experiments (Daunt *et al.* 1937) conducted in the infra-red however showed that at the transition to the superconducting state there was no change of the reflectivity in the pronounced manner expected. Additional experiments (London 1940, Pippard 1947 a, b, 1949, 1950) with microwaves lead to the same result, in fact there was a levelling off of the reflectivity as the temperature was decreased. The explanation for these results required a modification of classical theory. Beginning with the physical explanations of London and of Pippard, Reuter and Sondheimer (1948) went on to develop in a formal way the theory of the anomalous skin effect.

The explanation for the optical behaviour of metals at low temperature lies in the very long free path associated with conduction electrons. When the path is longer than the penetration depth of the electric field, the electrons no longer experience a uniform force between collisions. It is also true that the period becomes small relative to the mean time between collisions, but it is the long free path that provides the basis for the new theory. The complete theory shows that in the microwave region the nature of the reflection of the electrons at the surface is not significant being much the same for specular and diffuse scattering. In the optical region, however, diffuse scattering leads to a much greater difference from classical theory than does specular reflection. Although the name anomalous skin effect suggest a departure from the classical skin effect, it also shows that modification of the Drude theory is necessary. This was clearly demonstrated by the derivation of Holstein (1954) who used quantum mechanical methods together with physical arguments.

It is interesting to note the values of n/λ and k/λ predicted by the Drude theory for a good conductor at low temperatures. As shown in fig. 4 the maximum value of k/λ remains unchanged but the plateau is greatly extended toward longer wavelengths. It is evident that the wavelength range of 1 μ to 1 cm is removed from the skin effect region and even at 1 cm one could speak of the anomalous Drude theory rather than the anomalous skin effect.

In the extensive writings of Dingle (1953 a, b, c, d) it is shown in detail where the new theory departs most markedly from the old . There is little difference for transmission but a radical difference for absorbtivity. In terms of the optical constants, k is essentially the same in the old and the new but n is greatly changed. Referring to fig. 2, the absorbtivity $A(=1-R)$ is about 0·004 ; the new theory predicts 0·007, or about twice as much. The new value of n is likewise about two times that of the old. These values apply to the near infra-red ; they change somewhat with wavelength. It appears that the usual condition in the classical skin effect, namely that n and k are nearly equal, is no longer valid and that n is greater than k.

Fig. 4



Graph for Ag showing the wavelength variation of n/λ and k/λ as found by calculation using the Drude theory with the conductivity increased $\times 100$ over the normal room temperature value.

It is fortunate that the anomalous skin effect theory did not arrive earlier because older experimental work was in general not nearly good enough to check its predictions. The new theory has initiated new experimental work which indirectly lead to a better understanding of the older theory. It will be shown below that recent experiments are sufficiently accurate to prove that the new theory is essentially correct and that the Drude theory by itself is inadequate. Since the development of the theory is still in progress (Holstein 1954) it is not yet possible to make a final comparison with experiment. The study of the anomalous skin effect can be used to provide information on the nature of conduction electrons and is therefore of interest beyond the field of optics. In this paper, however, it will be used only as a refinement to the older classical theories.

§ 4. Fifty Years of Experiments

In addition to conceiving and applying the free electron model Drude also pioneered in the development of an experimental method (Drude 1902, Born 1943) for measuring n and k. His method, or some variation of it, has been used so widely that at least the essential features must be mentioned here : Parallel light, plane polarized at an angle of 45 degrees to the plane of incidence, is directed on the sample to be studied. The appropriate angle of incidence depends on the metal being studied, but it usually ranges from 70 degrees for poor conductors to near grazing for good conductors. Following reflection the light is in general elliptically polarized. Analysis of the nature of the ellipticity yields information which can be used to compute n and k. When suitable modifications have been made the method can be used in any wavelength range.

Without doubt the Drude method is extremely sensitive ; the problem is to make the sensitivity available for accurate measurements. This is not easy because of the complexity of the polarizing spectrometer, the instrument used in the method. To compensate partly for the complexity, the present day user has the benefit of many years of development of the instrument. Much of this development was made by those who have used the method to study the nature of thin corrosion layers where the method works extremely well because usually only relative values are required. The best evidence for the complexity is the fact that nearly everyone when beginning the use of the method seems called on to write one or more papers on the analysis of its operation. The problem of the preparation of samples is as difficult and as important as making optical measurements. In fact special studies have shown that most of the variation in experimental results can be traced to sample defects (Nathanson 1938, Beattie and Conn 1955 b). More or less standard metallurgical polishing methods were extensively used in the early days. For certain metals such as Ag this was almost permissible, but for other similar metals, Cu for example, it lead to gross errors. Fortunately progress has been made in devising methods of sample preparation, and some attention will be given to the matter later.

There are many dozens, perhaps even a few hundred, of experimental papers on the optical properties of metals. Their quality varies but nearly all claim fantastic accuracy. The actual accuracy becomes apparent when the results of several papers are compared. Values for k may vary by 10% or more, and values for n may differ by as much as a factor of four. Despite the great spread in results these old papers are of considerable value in that they make it possible to select metals which merit further attention. The very early papers tend to be more interesting because the authors had reasons for making the measurements : they wished to make comparisons with values obtained by computation using eqns. (4)–(6). As time went on measurements came to be made for no obvious reason, or only as an experimental exercise.

A search through many of these older papers has lead to the following conclusions : (1) If the goal is to find a metal which is most likely to follow the Drude theory over a long wavelength range, the evidence points toward liquid Hg as being the most promising metal. There are many measurements (Nathanson 1938, International Critical Tables 1926) in the visible region, some in the ultra-violet, and a few in the infra-red. Measurements have been made by Kent on other liquid metals (Kent 1919), mostly the kind that melts at low temperatures. The results suggest that these metals as a group follow the theory, but the measurements were confined to such a limited wavelength range that it is rather dangerous to generalize. Liquid alloys of these low temperature melting metals also tend to follow the theory, but again measurements are over only a limited wavelength range. (2) For the usual reasons alkali metals (solid) should be likely to follow the predictions of a free electron model. Measurements (Seitz 1941) in the visible and ultra-violet are in good agreement with the theory if the effective mass is used as an adjustable parameter. In the most recent work, which is probably the best, for at least one metal conclusions were based on only one sample (Ives and Briggs 1936, 1937 a, b). It would be worth the effort to repeat this work and extend the measurements into the infra-red. It seems that no measurements have ever been made on Li, solid or liquid. (3) For the 'good' monovalent non-alkali metals such as Ag, Au, and Cu there exist a great many measurements (International Critical Tables 1926). It is clearly shown that in the visible and ultra-violet there is no agreement with theory, but as the wavelength increases the difference decreases. Beyond about 2μ experimental k values tend to be only slightly low, but n values are several times too great. Some attention, but not much, has been given to solid alloys. (4) For the large group of multivalent metals some measurements have been made (International Critical Tables 1926). It seems clear that the difference between experiment and theory is much greater than the experimental error. These multivalent metals therefore tend to be of less immediate interest as subjects for study. Perhaps this situation will change later.

For the benefit of those readers who prefer to examine the older experimental results and then to form their own conclusions the following are the principal sources of n and k values :

(1) A large compilation by Valesck of values obtained before 1926 in the International Critical Tables (1926).

(2) A similar compilation (Physikalisch-Chemische Tabelln) together with some of the more recent values is given in Landolt-Bornstein.

(3) A book by Mayer (1950) on the physics of thin films.

(4) For values of significance for solid state physics books by Seitz (1941), and Mott and Jones (1936).

The most quoted values tend to be a sequence beginning with Voigt (1901), followed by Minor (1903), Meier (1910), Försterling and Fréedericksz (1913) and more recently by Kretzman (1940).

§ 5. APPROACH IN THE PRESENT PAPER

At the present time there is an urgent need for better experimental values of n and k. More accurate values make possible progress toward two broad goals : The first is to find the limits of validity of the Drude theory as given in eqns. (4) through (6). It was the original hope that perhaps all metals would follow this theory in some wavelength range. If the values of n and k for this range could be determined, then it might be possible to explain absorption in any other range as a combination of absorption by conduction electrons together with absorption due to other mechanisms. A second goal is to find experimental procedures which yield information of interest for solid state physics. The metals investigated were restricted to those having reasonably good electrical conductivity; semiconductors were not included.

There appeared to be no need to include in this paper a discussion of the development of the theory. The older work is available in textbooks (Seitz 1941, Mott and Jones 1936), the old together with the new has recently been reviewed by Ginsburg and Motulewitsch (1955). In addition the general problem of the mean free path of conduction electrons in metals has been reviewed by Sondheimer (1952). Great use of the existing theory was made in the design of the experiments. For example, mere substitution of numbers in eqns. (4) through (6) often yielded results not previously discussed. The theory of the anomalous skin effect will be treated as an extension of the Drude theory since it too deals with conduction electrons.

Every effort was made to avoid digressions into absorption mechanisms other than those based on the behaviour of conduction electrons. It was felt that the primary problem was to evaluate the Drude theory first. A slight deviation from this policy was the practice of making measurements on a sample over every wavelength range for which this could be done conveniently. Data of this kind will be of value later.

It is important to state clearly what was taken to constitute 'agreement of theory and experiment'. There are several degrees of agreement: (1) Complete agreement exists for a given metal when the experimental values of n and k for all wavelength regions agree to within the experimental accuracy with those calculated with eqns. (4)–(6). (2) There may be agreement for both n and k over a limited wavelength range. This will be taken to indicate that in regions with apparently no agreement there are mechanisms of absorption in addition to that associated with conduction electrons. (3) If agreement can be obtained in any wavelength range by adjusting the value of N/m^* in eqns. (4)–(6) this will be considered genuine agreement but less complete than (1) or (2) above. (4) If the difference between experimental and computed values of n and k in all wavelength regions exceeds the experimental error even after N/m^* has been used as an adjustable parameter, this will be considered no agreement. The absorption other than by conduction electrons may exist throughout the region in which eqns. (4)–(6) apply. When this is the case, a metal may be put into classification (4) falsely. It is conceivable that optical absorption by conduction electrons always follows the Drude theory and that any apparent disagreement is a consequence of failure to separate out the absorption due to other mechanisms. Some understanding is also necessary concerning the meaning of σ and of

N/m^*. σ will always be taken to mean the direct current conductivity and can therefore not be used as an adjustable parameter. To have agreement of theory and experiment the experimental value of σ as computed from optical measurements must be constant over an appreciable wavelength range, and this constant value must agree with values determined by electrical measurements. Occasionally experimenters have shown graphs in which the experimental value of σ is given as a function of wavelength. If this is done σ has a different meaning from the one used here; it is then just an empirical parameter.

It is well known that σ values determined from optical measurements are nearly always somewhat lower than bulk values for the metal in question. If the experimental value of n has the proper wavelength dependence but is high, this would tend to indicate the sample is defective in a way that decreases conductivity. However defects which reduce the d.c. conductivity as measured by electrical experiments can be different from those which reduce the optically determined value of σ. It is therefore dangerous to explain a low optical value of σ as due to sample defects without having some information concerning their nature.

It is difficult to give the meaning of N/m^* if its experimental value differs from the computed one. The practice adopted was to consider m^* an adjustable parameter and regard the difference between it and the free mass m as a measure of the departure from complete freedom of the conduction electrons. An alternate procedure is to use N as a parameter and call it the effective electron density. Whichever procedure is used it is required that N/m^* be a constant in the region where agreement is said to exist.

A survey of the older experimental work showed that if new work is to have any value it must be considerably better than the old. Therefore the policy was to restrict the scope of the experiments to the examination of a few representative metals and aim to achieve in fact the high accuracy that the older works usually claimed but did not have.

§ 6. DESCRIPTION OF EXPERIMENTAL METHODS

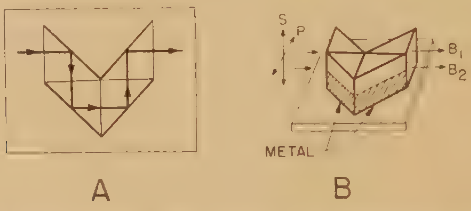
The Drude procedure for experimentally determining n and k requires a complicated piece of equipment. To avoid this disadvantage an effort was made to devise more direct methods requiring only simple equipment. In most cases the plan was to design attachments or special parts which could be incorporated into existing instruments. The essential features of several of the experimental procedures will be described.

6.1. *A Reflectivity Method Involving Intensity of Reflection at a 45° Angle of Incidence*

Determination of the intensity of reflection (as distinguished from amplitude of reflection) at normal incidence is one of the easiest measurements to conceive. Its disadvantage is that normal incidence cannot easily be achieved experimentally and ‘ near normal ’ is usually not permissible because it requires some knowledge of the state of polarization of the incident light. For this reason it was decided to use an angle of incidence of 45°.

To avoid corrosion and general contamination from the air, measurements were made at glass–metal, quartz–metal, and NaCl–metal interfaces (Schulz and Tangherlini 1954). Four right-angle prisms were arranged in the manner shown in fig. 5. A ray of light incident normally from the right in drawing A after four internal reflections leaves the opposite face unchanged in direction and without displacement. The lower half of each hypothenuse face was covered with an evaporated film of the metal being studied. A ray of light through the upper half of such a sample is totally reflected at glass–air interfaces. Therefore beam B_1 can be used as a reference against which to compare B_2 which is reflected at glass–metal interfaces. A necessary condition for the legitimate application of the equations of electromagnetic theory is that at a 45° angle of incidence R_p, the reflectivity in the p-plane of polarization, must equal the square of R_s, the reflectivity in the s-plane. To within the experimental accuracy all samples met this condition or were rejected.

Fig. 5



Drawings showing the optical path through a reflection sample. The prisms are close to one another but not in optical contact. Schulz and Tangherlini (1954).

All equations of classical optics concerned with the reflectivity of a metal assume that the interface of the metal with the neighbouring dielectric is a plane surface, and moreover it is assumed that the optical properties change discontinuously at the boundary. In practice a surface is sufficiently smooth when the roughness amplitude is small in relation to the wavelength of the light, let us say one five-hundredth of a wavelength. Such smoothness can be obtained at a glass–metal interface, but not at the free surface of a metal in contact with air. Whether or not the second assumption concerning a discontinuous change at the interface is satisfied is usually difficult to determine, but with the four-prism method used here a practical answer was easily arrived at. If any sort of gradient exists the necessary equality of R_p and R_s^2 will not be satisfied.

The metals studied were deposited from the vapour in a vacuum of 10^{-5} mm of Hg or lower, to a thickness of about 2000 A, i.e. considerably more than opaque. Every effort was made to keep the metal-prism interface as clean as possible. The metal charge to be evaporated was first prefused in an initial evacuation of the evaporation equipment. In the second evacuation during which the deposition occurred a movable barrier was placed in front of the prisms to intercept the initial beam of metal vapour. Deposition was as rapid as the equipment permitted which was about 1000 Å in 30 seconds. Following deposition the prisms were kept in a vacuum annealing furnace for a few days. The maximum temperature for metals of the kind Ag–Au–Cu was about 120°C. Higher temperatures caused a change that upset the required relation of R_s to R_p. The purpose of annealing was to remove the strains and crystal defects of every kind which are invariably produced in the condensation process. Ageing at room temperature was also effective, but it required about a year to go to completion.

Since the method being described measures intensity (not amplitude) of reflection it is not necessary to have extremely good prisms. It was essential however that they be free from defects which might depolarize the light. A working test was the following : When the incident light on a prism was polarized in the p-plane (or s-plane) and an analyzer in crossed position was placed after the prism the amount of light passing through the analyzer was less than 0·1%. Usually the prism defect which caused this depolarization was difficult to locate except when a knife-edge test was incorporated with the crossed Nicol test. A further test of the prisms was to compare the transmission in the s- and p-planes for glass–air–glass reflectivities. To within the experimental accuracy these were always equal. A visual Pulfrich photometer was an aid in locating any flaws in the material of the prisms. The four prisms shown in fig. 5 were secured to a metal base plate, an arrangement which permitted a sample to be turned about an axis parallel to the transmitted light beam.

It was necessary to look into the nature of reflectivity at non-normal incidence before a computation procedure could be devised. Figure 6 shows the manner in which R_s and R_p vary with angle of incidence for the case of the n, k and n_0 values indicated (approximately for silver in air at a wavelength of 5890 Å). The equations relating the various quantities are taken from König (1928) :

$$R_s = \frac{a^2+b^2-2a\cos i+\cos^2 i}{a^2+b^2+2a\cos i+\cos^2 i}, \qquad (10)$$

$$R_p = R_s\frac{a^2+b^2-2a\sin i\tan i+\sin^2 i\tan^2 i}{a^2+b^2+2a\sin i\tan i+\sin^2 i\tan^2 i}. \qquad (11)$$

The angle i is the angle of incidence. The two variables a and b are defined by the following equations :

$$a^2 = \frac{1}{2n_0^2}\{[(n^2-k^2-n_0^2\sin^2 i)^2+4n^2k^2]^{1/2}+n^2-k^2-n_0^2\sin^2 i\}, \qquad (12)$$

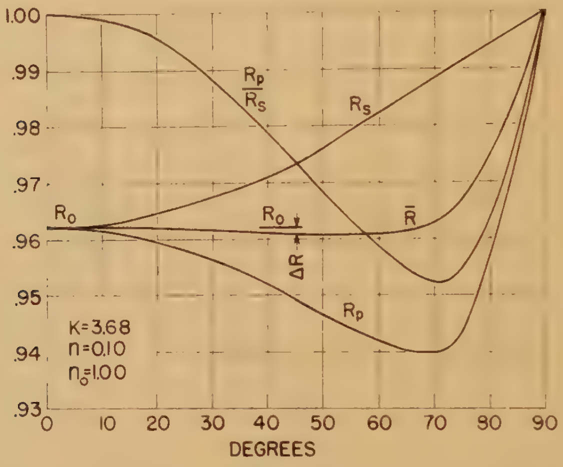
$$b^2 = \frac{1}{2n_0^2}\{[(n^2-k^2-n_0^2\sin^2 i)^2+4n^2k^2]^{1/2}-n^2+k^2+n_0^2\sin^2 i\}. \qquad (13)$$

For normal incidence ($i=0^\circ$) both R_s and R_p reduce to R_0 which is given by

$$R_0=\frac{k^2+(n_0-n)^2}{k^2+(n_0+n)^2}. \qquad (14)$$

It is evident at a glance that eqns. (10) and (11) are not in a form which permits easy computation. The procedure developed was one that related R_0 of eqn. (14) to R_s and R_p of eqns. (10) and (11). A preliminary step was that of defining a new reflectivity: $\bar{R}=\frac{1}{2}(R_s+R_p)$. The difference $\Delta R=(R_0-\bar{R})$ is always small relative to R_0 or $\bar{R}$ a condition which permits the use of $\bar{R}$ in eqn. (14) for obtaining preliminary values.

Fig. 6

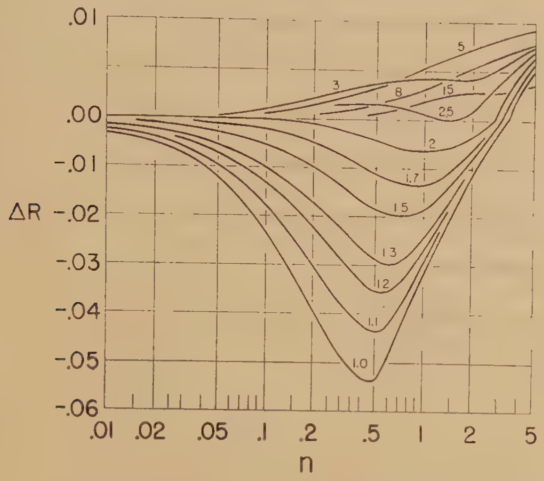


Graph showing the variation in reflectivities with changing angle of incidence for a particular set of values for k, n, and n_0. Note that at 45° the value of R_s^2 is equal to R_p. (n_0 is the index of refraction of the dielectric in contact with the metal.) Schulz and Tangherlini (1954).

For the metals studied a provisional value of k was obtained by an independent experiment. This k was used in eqn. (14) together with an experimental value of $\bar{R}$ to get a first value of n. Then n and k were used to find the value of ΔR. It is found convenient to prepare a set of values for ΔR such as those shown in fig. 7. With fig. 7 and eqn. (14) repeated approximations lead to accurate values of n. Multiple reflections between and within the prisms of a sample made it necessary to add corrections to the experimental values of $\bar{R}$ and R_s^2/R_p. These corrections were computed on the basis of intensity addition.

Several variations of the arrangement in fig. 5 were found convenient: It was possible occasionally to use only two prisms. This arrangement displaced the light beam, but the new position of the beam remained unchanged as the sample was moved perpendicular to the beam direction. Another variation was to change the position of the deposit on the hypothenuse face. Experimental details will be given at appropriate places below.

Fig. 7



Graph showing the values of ΔR as a function of n and k. The numbers on the curves indicate the k values. Note that the vertical scale for the positive ΔR region is different from that for the negative region. The calculations are for a vacuum–metal interface. To use the graph for the case of a dielectric other than vacuum, n and k must be divided by the index of refraction of the dielectric. Schulz and Tangherlini (1954).

6.2. *A Method for the Determination of the Absolute Phase Change ψ Accompanying the Reflection of Light*

In the conventional Drude procedure an experimental value is obtained for the difference $\Delta\psi$, between the phase change ψ_s in the s-plane and ψ_p the phase change in the p-plane of incidence. Usually the measurements are made near the principal angle of incidence where the difference $\Delta\psi$ is near its maximum value. In contrast, the method to be described presently (Schulz 1951 b, 1954 a) yields the absolute value of ψ at normal incidence (where ψ_s and ψ_p converge to a common value). Samples on which the measurements were made usually took the form of interference filters (Hadley and Dennison 1948) prepared by evaporation and deposition of the components in a vacuum. It was found advantageous to develop a comparison method for which Ag was selected as the reference metal.

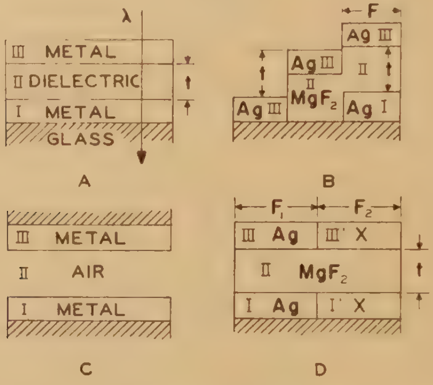
When light is reflected at normal incidence from the interface of a dielectric with an index of refraction n_0 and a metal with the optical constants n and k, the phase change ψ accompanying the reflection has a value given by eqn. (15).

$$\tan\psi = \frac{2kn_0}{k^2+n^2-n_0^2}. \qquad (15)$$

Figure 8 (*a*) shows schematically the essential parts of a filter used to determine ψ. The metal layers I and III are made of such thickness that about 1% of visible radiation would be transmitted by each separately. Layer II which forms the dielectric spacer must be sufficiently thick to give at least first order interference. The relation between a wavelength λ of light which is transmitted and the geometric thickness t of the dielectric is given by eqn. (16).

$$2n_0t/\lambda+\psi/\pi=N. \quad \text{(16)}$$

Fig. 8



Drawings which show diagrammatically the design of various type filters. Schulz (1951).

Methods (Scott *et al.* 1950, Schulz and Scheibner 1950) are available for accurately measuring t, λ, and n_0 (N is an integer equal to the order number of the interference). When t is sufficiently large, several wavelengths $\lambda \ldots \lambda_i$ will be transmitted. A relation between these wavelengths, independent of t, is given by eqn. (17) for the case of n_0 equal to unity for all wavelengths.

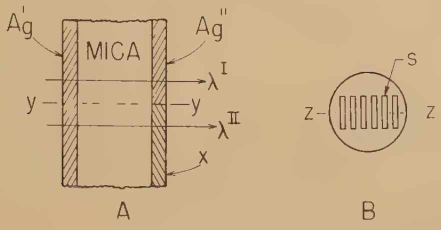
$$(N\lambda)_1-(N\lambda)_i=1/\pi[(\psi\lambda)_1-(\psi\lambda)_i]. \quad \text{(17)}$$

Usually n^2 in eqn. (15) is small relative to k^2, therefore only approximate values of n are required. For preliminary calculations such values of n can be obtained in conjunction with intensity of reflection experiments or from the literature when available.

For the study of Ag, filters of Ag–MgF_2–Ag, arranged as shown in fig. 8 (*b*), were made which had first order (N equal to unity) transmitted wavelengths in the range of 5500 Å to 6000 Å. In fig. 8 (*b*) part F represents the area forming the filter, and the remainder of the sample is used for the determination of the thickness t of the dielectric. The numbers I to III indicate the sequence in which the layers are deposited on a glass (or quartz) substrate. The geometry of the vacuum system for depositing the layers must be such that layer II of MgF_2 has a uniform thickness. Values of n_0 in the visible wavelength region for the MgF_2

spacer had been determined earlier (Schulz and Scheibner 1950). With such samples a value of 3·69±0·05 was obtained for k at the wavelength 5890 Å. This value for k was taken as a reference point for extending the measurements of k to other wavelengths. Filters of the type shown in fig. 8 (*c*) together with eqn. (17) were used for this purpose. Since an air gap formed the dielectric spacer the difficulty of determining the dispersion of a solid dielectric was avoided. Various size air gaps were used so that the interference order N, in the middle of the visible region varied from about 5 to 30. In fig. 8 (*d*) is shown an arrangement for measuring k_{x} of metal x relative to k_{Ag} for Ag. Two filters, F_1 and F_2 were formed. F_1 with the sequence Ag–MgF_2–Ag was used to determine the thickness of the MgF_2 deposit II which was common to both filters.

Fig. 9



Details of the filter construction and the arrangement for wavelength measurements. Drawing A shows the arrangement of components in a filter pair. Drawing B indicates how a survey was made of each sample by moving it with respect to the slit S of the spectrograph to a new position for each photograph. Schulz (1954 a).

In the comparison method as just illustrated (fig. 8 (*d*)) mica was found to be a much better dielectric material than MgF_2. Pairs of filters having a single mica sheet as the common dielectric spacer were made with the components arranged as shown in fig. 9 (*a*). On one side of a mica sheet assumed to have uniform thickness a film of silver Ag′ was deposited. Part of the opposite side of the mica was covered with silver Ag″ and the remainder with the metal x under investigation. The upper part of fig. 9 (*a*) with the Ag–mica–Ag sequence will be designated as filter I and the lower part with the Ag–mica–x sequence, as filter II. From the transmitted wavelengths λ^{I} and λ^{II} of such a pair of filters the absorption coefficient k_{x} of the metal x could be calculated.

The calculation procedure employed was similar to that used above, but complications arise here because of the dispersion of the mica. The relation of the wavelength λ^{I} to the mica thickness t, the mica index of refraction n_0, the order of interference N, and the phase change λ_{Ag} occurring during the mica–Ag–mica reflection is given in eqn. (18).

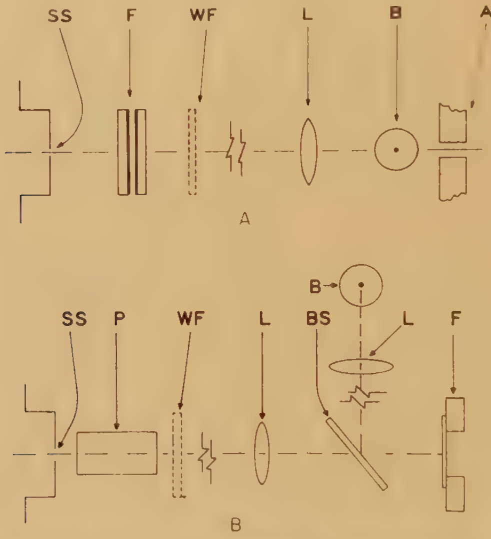
$$2n_0^{\mathrm{I}}t+\frac{\psi_{\mathrm{Ag}}^{\mathrm{I}}\lambda^{\mathrm{I}}}{2\pi}+\frac{\psi_{\mathrm{Ag}}^{\mathrm{I}}\lambda^{\mathrm{I}}}{2\pi}=N\lambda^{\mathrm{I}}. \qquad . \; . \; . \; . \; . \quad (18)$$

A similar equation can be written for λ^{II} which when combined with eqn. (18) leads to eqn. (19).

$$N(\lambda^{II}-\lambda^{I})-\left[\frac{\psi_{X}{}^{II}\lambda^{II}}{2\pi}-\frac{\psi_{Ag}{}^{I}\lambda^{I}}{2\pi}\right]$$
$$=\left[\frac{\psi_{Ag}{}^{II}\lambda^{II}}{2\pi}-\frac{\psi_{Ag}{}^{I}\lambda^{I}}{2\pi}\right]+2t(n_0{}^{II}-n_0{}^{I}). \quad . \quad . \quad (19)$$

In eqn. (19) the principal terms are to the left; those to the right are correction terms. The dispersion of mica was obtained in a preliminary experiment using filters of the type Ag–mica–Ag with the thickness varying from 1 μ to 30 μ. It was found that for a given wavelength the value of n_0 varied slightly from sample to sample, but the dispersion remained unchanged within the experimental error.

Fig. 10



The experimental arrangement for measuring wavelengths photographically: Arrangement A is used for transmission type filters and arrangement B for reflection filters. The Wratten filter WR (Kodak no. 22) was used to prevent overlapping spectra. In arrangement B the symbol BS identifies a beam splitter. The polarizer P eliminates multiple fringe patterns from double refracting mica. Schulz (1954 a).

Figure 10 shows the general features of the arrangements used for measuring wavelengths. Arrangement A was used for air filters of the type given in fig. 8 (*c*). A single filament incandescent lamp B provided illumination for forming the interference fringes while the iron arc A provided reference spectra for wavelength determinations. Illumination from A passed directly through B, therefore, no movement of the component parts was required. The sample F was placed as close to the slit SS of the spectrograph as was possible. Drawing B of fig. 10 is the arrangement for reflection filters. A definite advantage of reflection type samples is that they permit use of opaque layers (Ag″ and x of fig. 9 (*a*)) and thus eliminate any possibility of errors in ψ due to the metal layers being too thin.

The method works best on a grating spectrograph because of the uniform dispersion of this instrument. The upper wavelength limit is set at about 9000 Å by the photographic material now available. The lower wavelength limit is about 3500 Å and is determined by the transmission of mica or any other dielectric material used. The use of Ag as a reference metal is no limitation since the values of k for Ag obtained by all methods are nearly all in good agreement. It is not necessary that the mica used be completely free of cleavage steps. All that is required is that the area near the line y–y of fig. 9 (*a*) be relatively free from steps. To avoid errors due to steps, measurements were made at many positions across the sample as shown in fig. 9 (*b*).

6.3. *A Transmission Method for Obtaining Values of k*

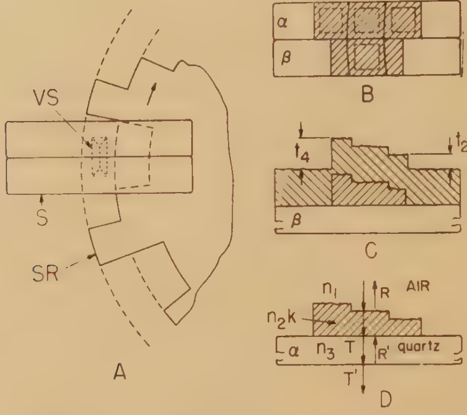
Although transmission methods have been used in the past (Murman 1933, Goos 1936, 1937, Simons 1943), they have always been less popular than reflection methods. This is partly a consequence of the many disadvantages of transmission methods : It is not easy to obtain the desired thickness of a deposit formed from the vapour ; the transmission for a suitable thickness is very small requiring a sensitive measuring instrument ; often different thicknesses are required for different wavelength ranges ; determining the thickness means an additional experiment and moreover this measurement is not easily made to the required accuracy ; and the sample must be of uniform thickness. There are additional disadvantages : the computations are often difficult because the films are of necessity less than opaque in thickness ; in general the samples can be used only for k determinations, other samples being required for a second type of experiment such as the intensity of reflection ; also, the transmission of the substrate may set the usable wavelength limits, both upper and lower.

There are however a few advantages which need emphasizing : The values of k obtained come closer to being the bulk values ; it is possible to minimize the effect of surface defects such as roughness ; recently the development of commercial equipment has reduced the necessity for building special instruments. Because of these advantages, it was felt that the transmission method was worth trying.

A detailed examination of the electromagnetic solution for transmission through a semi-transparent metal film was found helpful in designing appropriate samples (Schulz 1954 b). Suppose that the metal film is supported, and therefore bounded, on one side by a glass or quartz substrate and is bounded on the other side by air as shown in fig. 11 (*d*). Assume that monochromatic light of unit intensity is incident through air of index of refraction n_1 on to a metal film with constants n_2 and k.

When the thickness of the film is small enough a measurable intensity of light T emerges into the substrate of index n_3. The experimentally measured intensity T' which passes through the substrate is smaller than T because of internal reflections within the substrate. The exact

Fig. 11



Drawings showing experimental details. In A the substrates S were placed as close as possible to the stepped rotor SR. The distance from the vapour source VS to the substrates was 25 cm. In B the shaded area is that over which metal was deposited; the dashed squares show the regions in which transmission was measured. In C and D the surface of the metal has been drawn rough to approximate the actual situation. The meaning of the symbols used in D is given in the text. Schulz (1954 b).

solution for T in fig. 11 (d) is rather clumsy algebraically, therefore only the approximation for large thicknesses will be given here:

$$T = C \exp(-4\pi kt/\lambda), \qquad \qquad (20)$$

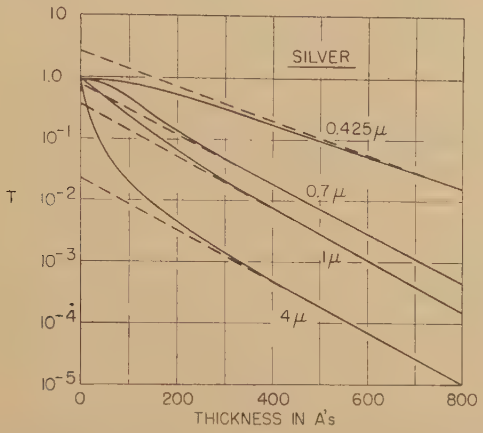
where

$$C = \frac{16 n_1 n_3 (n_2+k)^2}{[(n_2+n_1)^2+k^2][(n_2+n_3)^2+k^2]}. \qquad \qquad (21)$$

An examination of the derivation of eqn. (21) shows that the exponential term arises from the absorption in the metal film and that the pre-exponential C is associated with reflections at the film boundaries.

The special features of optical transmission by a metal can most easily be shown graphically using semilog paper. Figure 12 gives calculated values of the transmission of Ag for various wavelengths and for thicknesses up to 800 Å. In contrast to the usual optical absorption of materials other than metals, pure exponential absorption does not occur for thin samples but sets in only after the thickness exceeds about 400 Å. Each curve in fig. 12 has two principal features, a slope and an extrapolated intercept. Comparing the graph with eqns. (20) and (21) the slope is associated with the exponential and the intercept at zero thickness with the pre-exponential C. Because of this behaviour of metals one set of measurements yields two values of k: The first and most important is that found from the slope; it gives k_i for the interior. In addition, the extrapolation to zero thickness leads to a second value of k, that is k_s, for the surface. Surface defects tend to reduce k_s to values lower than those for k_i.

Fig. 12



Transmission T versus thickness of Ag for several wavelengths. The broken lines are extensions of the linear portions of the curves; their intersections on the vertical axis (for zero thickness) define the C values of eqn. (21). (In making the calculations for this graph preliminary values of n and k were used; final values are given in table 3, table 5, and fig. 23.) Schulz (1954 b).

The graph of fig. 12 suggests that a series of samples of increasing thickness beginning at about 350 Å would best define the slope associated with pure exponential absorption and leading to a value for k_i. The design of the samples actually used is given in fig. 11. These samples were prepared by condensation from the vapour. Three thicknesses of the metal were deposited simultaneously on to a pair of quartz substrates, alpha and beta. By means of a rotating shutter the thicknesses were made in the exact ratio of 2 : 3 : 4. One component called alpha was used for transmission measurements and the other component, beta, was reserved for thickness determinations. These thicknesses were usually in the neighbourhood of 700 Å to 800 Å for t_4 and were measured by an interference method (Scott *et al.* 1950) after an additional layer of Ag had been added as shown in fig. 12 (*c*). Since the rotating shutter was virtually perfect relative to the optical measurements, the thickest deposit t_4 and the thinnest t_2 should be in the ratio of two to one. To within the experimental accuracy of ±7 Å this was the case.

6.4. *Other Recently Developed Experimental Techniques*

The methods just considered were described in some detail because they were used to obtain most of the results to be presented below.

These methods are not necessarily the best. but they are dependable as indicated by the results obtained over a period of years. Also they illustrate the new methods made possible by recent progress in technology. Following are some of the main divisions of this technical development :

1. Electron microscopy (Zworykin *et al.* 1945) and electron diffraction (Pinsker 1953) have shown the structure of evaporated films (Picard and Duffendack 1943, Levinstein 1949, Sennett and Scott 1950) and the mode of growth (Schulz 1949). Several books are available on the physics of thin films (Mayer 1950, Heavens 1955), as well as a review article (Schopper 1954).

2. The use of evaporated films in the optics industry has resulted in improved methods of producing them. Interference optics has also contributed (Wolter 1956, Kuhn 1951).

3. A great variety of optical measuring techniques has been described (Scott *et al.* 1950, Tolansky 1948, Zernike 1950). Some are of general interest, others are special. The merit of each depends on the situation.

4. Interference optical techniques directly related to determining optical constants have been developed by Fleischmann (1951), Schopper (1951 a b, 1952 a, b, 1953, 1955) Fleischmann and Schopper (1951 a, b, 1952) and Fleischmann and Lohmann (1954).

5. The Drude technique has been analyzed and modified with special interest for application in the infra-red (Conn and Eaton 1954 a, b, c, d, Beattie and Conn 1955 a, Beattie 1955, Robinson 1952, Avery 1952, Simon 1951, Anchard *et al.* 1952 and Hodgson 1955).

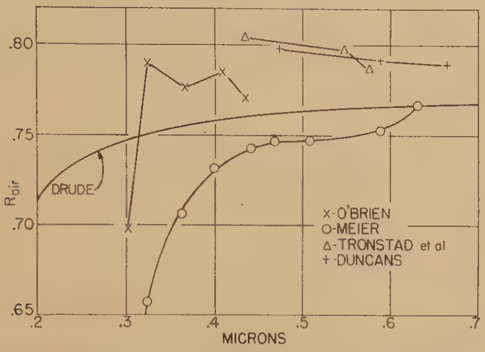
6. Etching techniques developed in metallurgy provide new methods of preparing samples. Electropolishing is a promising development although somewhat erratic at the present time (Tegart 1956).

§ 7. Recent Experimental Results

7.1. *Liquid* Hg *and Liquid* Ga

To present at the outset a strong case for the validity of the Drude theory, the experimental results for liquid Hg and liquid Ga will be discussed first. As indicated earlier in § 4 the measurements which were made in the past tended to show agreement of theory and experiments (Meier 1910, Drude 1890, Erochin 1912, Duncan and Duncan 1913, O'Brien 1926, Tronstad and Feacham 1934, Lange 1935). In fig. 13 are given several values of reflectivity computed from experimental values of n and k together with values calculated from the Drude theory. These results suggest that if the measurements were carried out with superior methods the agreement might be made complete over all wavelength regions. For the most part the older work was confined to the visible and ultra-violet regions. The experimental results now to be described (Schulz 1957 a) will show that the Drude theory is valid to within the experimental accuracy from $0{\cdot}3\,\mu$ to $10\,\mu$ for both liquid Hg and liquid Ga at room temperature (25°c). Drude values of n/λ and k/λ have already been given in fig. 3 for Hg; values for Ga may be found in fig. 14.

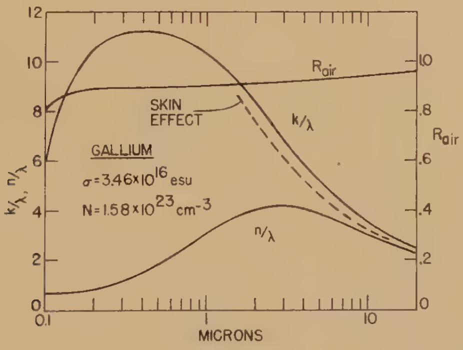
Fig. 13



The reflectivity R_{air} at a Hg–air interface for normal incidence. These values for R_{air} were computed from the n and k values given in Meier (1910), Duncan and Duncan (1913). O'Brien (1926), Tronstad and Feacham (1934). Schulz (1957 a).

Intensity of reflection measurements were made at glass–metal, quartz–metal, and NaCl–metal interfaces using the four-prism method discussed in connection with fig. 5. Although the method was the same, the sample design was slightly different. In place of application by evaporation the liquid metals were held against the hypothenuse face with a plastic cup. To form a clean interface of the metal and prism the liquid was in most cases poured in a vacuum. The good quality of the interface was indicated by the equality of R_s^2 and R_p. Because of the low reflectivity of Hg and Ga as compared with Ag only one prism formed the sample, the other three being replaced by three mirrors.

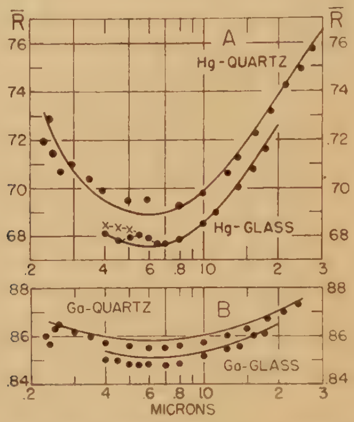
Fig. 14



Graph showing the values of n/λ, k/λ, and R_{air} for Ga. The values of σ and N used in the computations are shown on the graph. Schulz (1957 a).

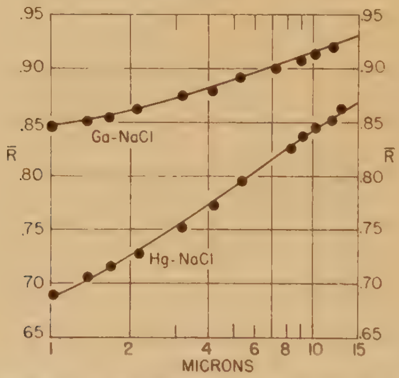
Measurements in the range of 0·23 μ to 0·80 μ were made on samples of glass and quartz with a Beckman Spectrophotometer to which suitable attachments had been made to accommodate the samples. For wavelengths above 0·35 μ a Glan–Thomson prism was used to polarize the light. When using a quartz prism for the region of 0·23 μ to 0·40 μ a block of $CaCO_3$ was used as a polarizer and a moveable slit employed to select either the O or E beam. Measurements in the infra-red, 1 μ to 10 μ, were made with a Perkin–Elmer Model 13 Spectrometer using single beam optics.

Fig. 15



Reflectivity values for samples using glass or quartz prisms. The solid lines were obtained with the Drude theory ; the solid circles are experimental values. For Hg–glass samples the crosses are values from prisms which were given a different cleaning treatment. Schulz (1957 a).

Fig. 16



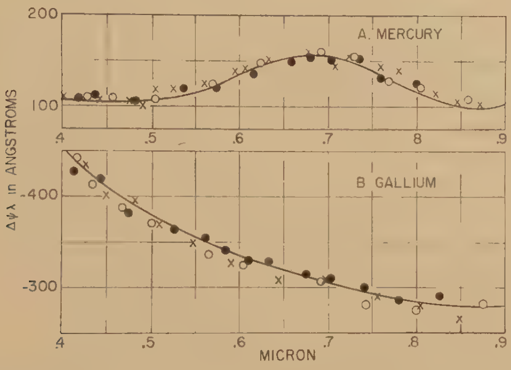
$\bar{R}$ values for samples using NaCl prisms. Solid lines were obtained with the Drude theory ; the solid circles are experimental values. Schulz (1957 a).

Experimental results for glass and quartz prisms are given in fig. 15 and for NaCl prisms in fig. 16. The solid lines are values predicted by the

Drude theory and the points are experimental values. On the whole the agreement is good, but there is a consistent tendency for the experimental values to be low. In addition to this there are several local irregularities: For both Hg and Ga in the ultra-violet below 0·3 μ there is scattering of points probably due to experimental difficulties such as low light intensity. For Hg there was a slight maximum at 0·55 μ that changed somewhat depending on the method of sample preparation. Less accuracy was possible with NaCl prisms because of the difficulty in polishing NaCl. Comparison of fig. 13 with figs. 15 and 16 shows the improvement in experimental accuracy.

A second type of experiment was that of measuring with the method described in fig. 9. The unknown metal labelled x in the figure was now the liquid Hg or the liquid Ga, the liquid being held against the mica in a plastic cup. The quality of the mica–metal interface was more critical here than in the case of intensity of reflection experiments. It was discovered that a thin film of Ag was an excellent wetting agent for Hg. Some idea of the accuracy attained is shown in fig. 17 where again the solid lines indicate computed values and the various symbols are for experimental values.

Fig. 17



Representative results of phase change measurements. In graph A are shown $\Delta\psi\lambda$ values for several samples for Hg relative to Al, while graph B gives similar results for Ga relative to Ag. Schulz (1957 a).

From the measurements presented in figs. 15, 16, and 17 experimental values for n and k were computed. They are listed in table 1 together with values predicted by the Drude theory. The differences are nearly always less than the experimental error. A second method of comparison which averages all values between 0·4 μ and 0·87 μ is given in table 2 for σ and N.

The main conclusion from these experiments is that for liquid Hg divalent) and liquid (Nathanson 1936) Ga† (trivalent) the Drude theory is quantitatively correct in the wavelength region 0·4 μ to 0·87 μ. From reflectivity measurements alone the evidence in fig. 15 suggests that the theory is also valid from 0·4 μ down to 0·25 μ. From fig. 3 for Hg and fig. 14 for Ga it is clear that beyond about 2 μ the Drude theory passes

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† These measurements on liquid Ga seem to be grossly incorrect.

Table 1. Comparison of Values of n and k Predicted by the Drude Theory with Values Obtained Experimentally. The Probable Errors in the Experimental Values of n and k are 4% and 2% respectively

λ	Mercury				Gallium			
	n		k		n		k	
	Drude	Exp	Drude	Exp	Drude	Exp	Drude	Exp
0·40	0·741	0·73	3·021	3·01	0·576	0·59	4·55	4·50
0·50	1·072	1·04	3·703	3·70	0·876	0·89	5·67	5·60
0·60	1·430	1·39	4·315	4·32	1·225	1·25	6·73	6·60
0·70	1·798	1·76	4·858	4·83	1·625	1·65	7·73	7·60
0·80	2·176	2·14	5·347	5·33	2·060	2·09	8·68	8·50
0·87	2·436	2·40	5·654	5·63	2·375	2·40	9·37	9·20

Table 2. Comparison of the Values of σ and N given in Tables of Physical Constants with the Values Obtained Experimentally

Metal	$\sigma \times 10^{-15}$ e.s.u.		$\sigma_{\mathrm{exp}}/\sigma_{\mathrm{tables}}$	$N \times 10^{-22}$ cm^{-1}		$N_{\mathrm{exp}}/N_{\mathrm{tables}}$
	Tables	Exp		Tables	Exp	
Hg	9·35	9·4±0·2	1·01±0·02	8·14	8·0±0·2	0·98±0·03
Ga	34·6	33·4±0·6	0·97±0·03	15·8	15·4±0·4	0·98±0·03

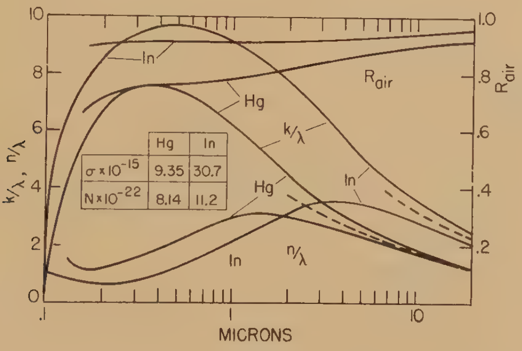
into that for the classical skin effect where σ alone determines the optical properties and N is of no significance. A measurement of emission at 25·5μ by Hagen and Rubens (1903) was in excellent agreement with the skin effect theory: The experimental result is 0·0755 and the theoretical value 0·0766 (reflectivity is equal to unity minus emission). The only wavelength region where the theory has not been tested at all is in the ultra-violet below 0·25 μ. It would be of interest to see whether or not the high predicted reflectivity of liquid Ga in this region actually occurs.

The results for liquid Hg and liquid Ga are consistent with the generalization suggested by the experiments of Kent (1919) that all low temperature melting metals when in the liquid state obey Drude's theory. On the other hand, when these metals are solid they do not follow the theory. For high temperature melting metals, Au and Cu, for example, the optical properties for the liquid state, at least in the visible region, are very different from those predicted by the Drude theory. This can be seen by direct visual inspection. It appears therefore that the optical properties in the visible region for these two metals in the liquid and solid states are similar.

7.2. *Liquid Alloys* (Hg–In), (Hg–Tl), *and* (Ga–In)

The results for liquid Hg and liquid Ga which have just been described suggested additional experiments with liquid alloys. The obvious first choice would be a mixture of Hg and Ga, but these two metals are completely immiscible (Hanson 1936). A search showed that at room temperature only a few metals dissolved to any extent in either Hg or Ga (Hanson 1936). The combinations selected were (Hg–In), (Hg–Tl), and (Ga–In). The experiments were confined to intensity of reflectivity measurements because these were adequate for the goal which was to find the extent of agreement of the experimental results with the Drude theory. A large part of the effort was given over to measuring electrical conductivities since these were usually not available in the literature. In the computation of N it was assumed that each atom in an alloy gives up a number of conduction electrons equal to its usual chemical valence. The most important result was that the optical properties of liquid alloys do not in general follow the Drude theory (Schulz 1957 b).

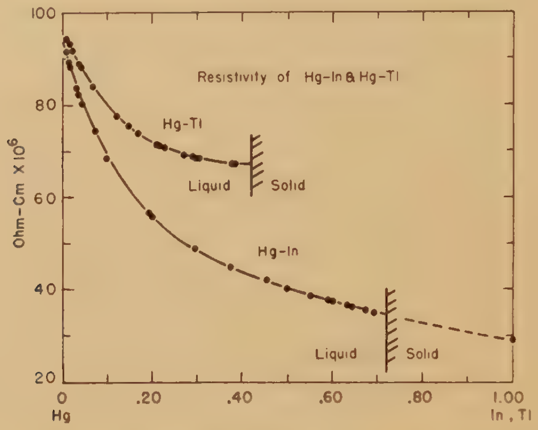
Fig. 18



Graph showing calculated values for k/λ, n/λ, and R_{air} for pure Hg and pure In. Values of σ (d.c. conductivity in e.s.u.) and N (electrons per cm^3) used in the calculations are shown in the table. Indium is assumed to be in the supercooled state at 25°c. Broken lines are used to show results obtained from the classical skin effect theory. Schulz (1957 b).

For several reasons the most interesting alloy was Hg–In: (1) The components have different chemical valences, two and three respectively. (2) Their electrical properties, σ and N, are appreciably different. (3) The computed reflectivities are quite different (see fig. 18). (4) The alloy exists as a liquid over a wide composition range—up to 72 atm % In at room temperature (Spicer and Banick 1952). In fig. 19 are shown experimental values for specific resistivity as a function of composition. An interesting feature is the extrapolation to 100% In : If In could be supercooled to room temperature, and if the temperature coefficient of resistivity (Scala and Robertson 1953) is here the same as above the melting temperature, then the computed resistance in this condition falls on the extrapolated curve.

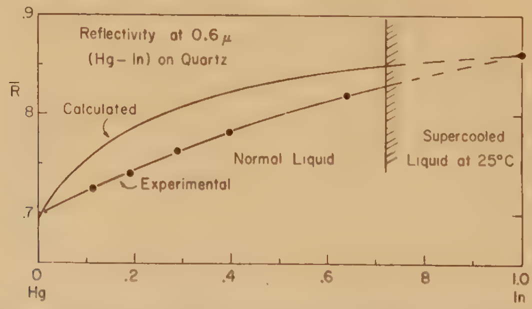
Fig. 19



Resistivity of (Hg–In) and (Hg–Tl) as a function of composition at 25°c.

The experimental method for measuring the intensity of reflectivity was that given in fig. 5 and the arrangement the same as used for Hg and Ga. Usually a rather large capacity cup was held against the hypothenuse face of a right angle prism and the composition was varied by successive additions of the solid component. The prism material

Fig. 20

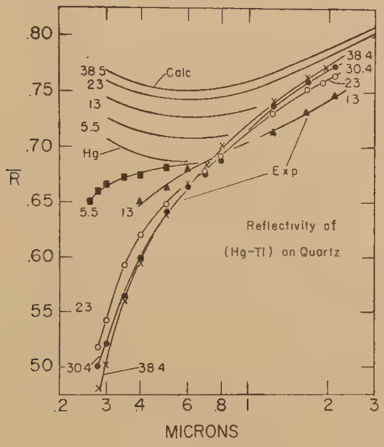


Graph showing calculated and experimental values of the reflectivity $\bar{R}$ for (Hg–In) on quartz for In compositions of 0 to 72 atm %. For compositions beyond 72 atm % the calculated values assume the (Hg–In) alloy to be in the supercooled state at 25°c. (No experimental values were possible in the hypothetical supercooled range.) Schulz (1957 b).

was varied for the different wavelength regions under study. Measurements were made on a Beckman Spectrophotometer and a Perkin–Elmer infra-red spectrometer.

In fig. 20 are given results for 0·6 μ which are typical for the wavelength region of 0·3 μ to 1 μ. The experimental measurements are consistently lower than the values calculated for the Drude theory. As might be expected the extrapolated curves intersect at 100% In suggesting that liquid In itself is a Drude type metal. For wavelengths longer than 1 μ the difference between experimental and calculated values diminishes and at 10 μ in the pure skin effect region becomes zero. The difference between the two curves in fig. 20 is of a kind that cannot be removed by adjustment of the effective mass.

Fig. 21



Graph showing calculated and experimental values of the reflectivity $\bar{R}$ for (Hg–Tl) on quartz. The atomic per cent of Tl in the alloys is indicated by the figures on the curve. Schulz (1957 b).

The second alloy studied (Hg–Tl) again is a combination of a divalent and a trivalent metal, but the solubility limit at room temperature is only 42 atm % Tl (Hanson 1936). Also Tl is an unpleasant material to handle. The results of intensity of reflection measurements given in fig. 21 again show a decided difference between experiment and theory but of a much different character than for (Hg–In).

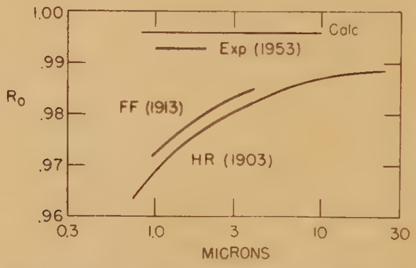
A third alloy studied, that of (Ga–In), was not an interesting combination as both metals are trivalent and the calculated reflectivity of each component is nearly the same value. Experimentally it was found that the reflectivity was independent of the composition of the alloy.

Preliminary measurement on the reflectivity of pure liquid In has shown that to within the experimental accuracy of plus or minus 1% the results are in agreement with the Drude theory. It follows that when two liquid metals each of which follows the Drude theory are combined the resulting alloy does not necessarily follow the theory. This conclusion is somewhat different from that of Kent who seems to have found alloys which do follow the theory (Kent 1919).

7.3. *Solid* Ag, Au, *and* Cu

These three similar monovalent metals are relatively easy to handle and largely for this reason have been among the favourite metals studied in the past. Although not so simple as the alkali metals they are truly ' metallic '. All three of the principal experimental methods outlined above were used to determine n and k, the measurements covering the range of about 0·3 μ to 3 μ. The general conclusion from the work was that for wavelengths greater than about 2·5 μ two metals, Ag and Au, follow the Drude theory, but for Cu it is necessary to assume a value of 1·45 for m^*/m to bring about agreement of theory and experiment.

Fig. 22



Graph showing the reflectivity R_0 at a metal–air interface for Ag as a function of wavelength. HR and FF refer to Hagen and Rubens (1903) and Försterling and Fréedericksz (1913), respectively. Schulz (1954 a).

Reflectivity measurements were made on the four-prism type samples shown in fig. 5. Reflectivities thus obtained were used together with k_i values in eqn. (14) to compute n values. The new values of n were almost always much lower than those published earlier (International Critical Tables 1926). This is attributed to the protected interfaces (dielectric-metal) and the annealing treatment of the samples. In the range of 1 μ to 2 μ the calculated reflectivity for normal incidence at a Ag–metal interface is constant at 0·993 as shown in fig. 22. Also shown is the value 0·996 obtained from the Drude theory and two sets of experimental values commonly quoted (Hagen and Rubens 1903, Försterling and Fréedericksz 1913). The difference of 0·003 between the new experimental value and that required by theory is approximately that predicted by the anomalous skin effect. Therefore it is concluded that theory and experiment are now in agreement to within the experimental uncertainty of about ±0·001, at least for the case of Ag. Similar reflectivity measurements were made on samples of Au and Cu with the results shown in table 3. Those for Cu are in a reasonable agreement with the theory, but those for Au are low by 0·006. No explanation has been found for this low value for Au. In table 3 values for n are given in the form n/λ^2 because this quantity is a constant in the wavelength region under study (λ is in micron units). (The reflectivity of Ag at low temperatures will be treated in § 7.4.)

Table 3. Table showing various Experimental and Calculated Quantities for Ag, Au, and Cu for a Wavelength of 2 μ. The Experimental Value of n/λ^2 was obtained using the Experimental Value of R_0 plus the Anomalous Surface Correction of 0·003.

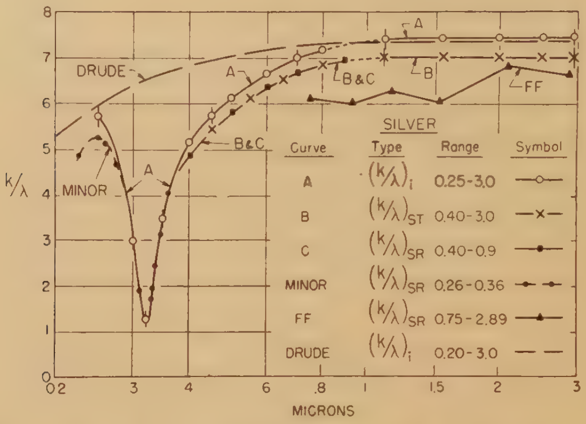
Metal	Concerning R_0		Concerning n/λ^2		Concerning $(k/\lambda)_i$		
	Exp plus 0·003	Free el'n calc	Exp	Free el'n calc	Exp	m^*/m	k_{ST}/k_i
Ag	0·996	0·996	0·050	0·050	7·45	0·97	0·94
Au	0·988	0·994	0·140	0·070	7·40	0·98	0·94
Cu	0·995	0·996	0·062	0·050	7·30	1·45	0·86

Because the results of Hagen and Rubens (1903) have been so widely quoted several errors must be pointed out in their work. In calculating the reflectivity of Ag they assumed that at 25·5 μ the classical skin effect theory is applicable which is equivalent to assuming that n is equal to k. This is far from the truth, as can be seen from fig. 2. The low computed reflectivity thus obtained was in agreement with the low experimental value shown in fig. 22. It was erroneously concluded that the classical skin effect theory is valid at 25·5 μ. This same error occurs in their work for all good conductors but not for poor conductors such as Hg (see fig. 3). (The measurements by Hagen and Rubens at 25·5 μ were made at 170°C. It is not easy to convert these measurements to room temperature conditions.)

Turning now to transmission experiments, experimental and calculated values of k/λ for Ag are shown graphically in fig. 23. To aid in distinguishing the various values, a key is included in which the symbols have the following meaning : i indicates an internal value obtained from the slope of the curves such as those in fig. 12 ; ST indicates a surface value obtained by a transmission experiment from the intercept at zero thickness as in fig. 12 ; SR indicates a surface value obtained by reflection experiment, for example, for curve C through the measurement of ψ. (No experimental measurements could be made in the interval 0·8 μ to 1·1 μ—this is the meaning of the broken section in curves A and B.) The most important feature of the graph is the close agreement of the curve for the Drude values and curve A for the bulk experimental values.

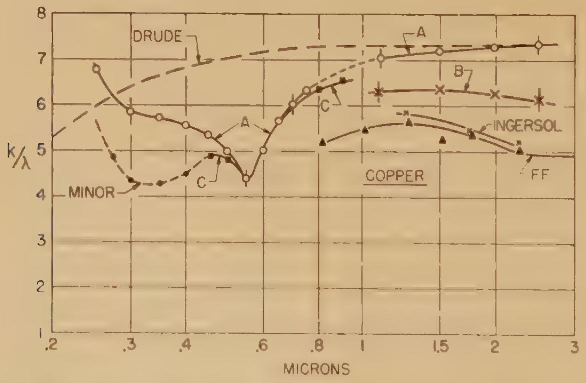
There is good agreement of the surface values ST and SR between 0·4 μ to 0·9 μ where the curves B and C almost coincide. Both of these surface values are lower than the internal values given in curve A, although there are indications that all three curves A, B, and C tend to unite below 0·4 μ. Experimental values below 1 μ are of no immediate interest except to show that in the ultra-violet region near 0·25 μ there is again a tendency toward agreement of experiment and theory. The pronounced

Fig. 23



Graph showing various k/λ values for Ag as a function of wavelength. Probable experimental errors are indicated by vertical lines. FF refers to Försterling and Fréedericksz (1913). Schulz (1954 b).

Fig. 24



Graph showing various k/λ values for Cu as a function of wavelength. The code for labelling is approximately the same as that for fig. 23. In some cases the range is different as can be seen directly from the graph. In the calculations to obtain the curve labelled ' Drude ', m^* was taken equal to 1·45 m. Schulz (1954 b).

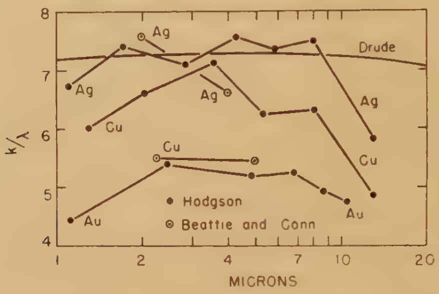
disagreement centred at 0 325 μ is evidently due to effects in addition to those associated with conduction electrons.

For the case of Cu agreement between experimental values and Drude values for k_i could be secured only if it were assumed that m^*/m had a value of 1·45. Experimental results are given in fig. 24 where the symbols have the same meaning as in fig. 23. Since the minimum at 0·55 μ is at a higher wavelength than that for Ag, the levelling off of curve A in the infra-red does not occur until about 2·5 μ. Cu is a much more reactive metal than Ag; therefore, one might expect errors when measurements are made on air-exposed surfaces. Curve B for ST. for example, which involves measurements on one air–metal surface and on one quartz–metal interface is decidedly lower than curve A, while curve C for SR based on measurements at a metal–mica interface is only slightly lower than A and therefore tends to resemble the situation for Ag. Also, as was true for Ag, curves A and C for Cu tend to become identical at or near the minimum. The two older sets of measurements by Ingersol (1910) and by Försterling and Fréedericksz (1913) made on air-exposed surfaces are considerably lower than any of the new measurements. It is evident that more effort is required in the ultra-violet region for Cu. Measurements on Au samples gave results similar to those for Ag. A summary of the results for k_i and k_{ST} is given in table 3 for all three metals Ag, Au, and Cu. Some further conclusions and remarks suggested by the experimental results will now be considered.

The theory of Drude, as well as all other theories of solids, is concerned with the interior of a metal but of necessity any optics experiment, even a transmission experiment, involves reflection and therefore surface effects. The value of k designated by k_i comes close to being the bulk value but is not completely independent of surface effects. It follows that even this experimental value would tend to be lower than the bulk value. Samples were made with t_4 of fig. 11 (*d*) near 1000 Å, but these samples gave the same results as those with thicknesses near 600 Å. This result would tend to indicate that the experimental k_i value is within the experimental error of being the true bulk value. The reason for the large difference of 6% between k_i and k_{SR} and k_{ST} in fig. 11 is not definitely known. It could be due in part to a fundamental reason not yet understood, or to surface defects such as roughness. Inspection of older experimental work shows that here too k values obtained by transmission experiments were nearly always higher than those obtained by reflection experiments (Murman 1933, Goos 1936, 1937).

Two additional sets of measurements on Ag and Cu in the infra-red have recently been reported (Beattie and Conn 1955 b, Hodgson 1955). In both cases the wavelength range was extended to somewhat beyond 10 μ and the measurements were made on air–metal surfaces with a polarizing spectrometer. Because of the type of sample used (air exposed), n values obtained were high and the computed conductivities were low especially for the corrosive metal Cu. One might expect the chief value of the experiments to be that of obtaining k values for long wavelengths. Unfortunately, as shown in fig. 25, the scatter in each set, and the difference between the two sets of values, are too great for one to have confidence in either set of measurements. Beattie and Conn (1955 b) found indications for a resonance at 7 μ for Ag, but Hodgson (1955) apparently did not find any evidence of this kind. For wavelengths greater than 1 μ there is little reason to expect effects other than those due to conduction electrons but only experiments will prove whether or not this is definitely true. The transmission method (§ 6.3) becomes unsatisfactory beyond about 3 μ; therefore, at this time there is no method other than that used by Beattie and Conn, and by Hodgson for wavelengths longer than 3 μ. Beattie and Conn have compared results from several types of samples. The results for evaporated films seem to be more nearly in agreement with values given by the transmission method.

Fig. 25



Experimental results for k/λ. Values for Beattie and Conn (1955 b) are taken from table 5 of their paper; values for Hodgson were supplied through personal communication.

Table 4. Comparison of Various m^*/m Values. For the items entered under 'Other optical experiments' m^*/m was taken equal to the quotient of the Chemical Valence Divided by the Experimental Value of the Electrons per Atom

Metal	Present investigation	Other optical experiments			Electronic specific heat	
		(1)	(2)	(3)	(4)	(5)
Ag	0·97	1·07	1·11	0·93	1·18	0·96
Au	0·98	1·13	—	1·88	—	1·16
Cu	1·45	2·56	2·44	1·64	1·47	1·38
Al	—	—	2·34	2·22	—	—

(1) Försterling and Fréedericksz (1913); (2) Beattie and Conn (1955 b); (3) Hodgson (1955); (4) Rayne (1954); (5) Corak *et al.* (1955).

In addition to testing the validity of the Drude theory optical experiments on Ag, Au, and Cu also give information concerning the nature of conduction electrons, in particular their effective mass m^*. Various values of the ratio m^*/m are given in table 4. It is interesting to compare the values obtained from optics experiments with those computed from specific heat determination (Rayne 1954, Corak *et al.* 1955). Agreement is sufficiently close to show that the respective values must be concerned with essentially the same quantity. For example, values for Cu are in both cases quite different from those for Ag and Au.

The n and k values in the visible region for Ag, Au, and Cu show pronounced departures from values predicted by the Drude theory but these metals have been given so much attention in the past that for historical and practical reasons it seems worthwhile to give the results of recent measurements (Schulz and Tangherlini 1954, Schulz 1954 a). The values listed in table 5 are in good agreement with another set given by Weiss (1948). The agreement is more than usually significant because quite different experimental methods were used in each case. Givens (1955), however, questions the correctness of the results for Cu because of a possible effect of inadequate vacuum during preparation of samples.

Table 5. Table giving n and k Values for Ag, Au, Cu, and Al in the Wavelength Range of 0·4 μ to 0·95 μ

Wavelength	Optical Constants							
	Silver		Gold		Copper		Aluminium	
(Å)	n	k	n	k	n	k	n	k
4000	0·075	1·93	1·45	—	0·85	—	0·40	3·92
4500	0·0[illegible]5	2·42	1·40	1·88	0·87	2·20	0·49	4·32
5000	0·050	2·87	0·84	1·84	0·88	2·42	0·62	4·80
5500	0·055	3·32	0·34	2·37	0·72	2·42	0·76	5·32
6000	0·060	3·75	0·23	2·97	0·17	3·07	0·97	6·00
6500	0·070	4·20	0·19	3·50	0·13	3·65	1·24	6·60
7000	0·075	4·62	0·17	3·97	0·12	4·17	1·55	7·00
7500	0·080	5·05	0·16	4·42	0·12	4·62	1·80	7·12
8000	0·090	5·45	0·16	4·84	0·12	5·07	1·99	7·05
8500	0·100	5·85	0·17	5·30	0·12	5·47	2·08	7·15
9000	0·105	6·22	0·18	5·72	0·13	5·86	1·96	7·70
9500	0·110	6·56	0·19	6·10	0·13	6·22	1·75	8·50

7.4. *Reflectivity Experiments at Low Temperature*

Following the development of the theory of the anomalous skin effect experiments were performed for the express purpose of testing the new theory. Among the first was that of Ramanathan (1952) who found the absorption A, of Cu at 4·2°K to be 0·0062 for radiation in the neighbourhood of 14 μ. This result was not satisfactory since the theory predicted a value of 0·003. Recently Biondi (1956) has carried through much more refined experiments, therefore, the discussion will deal with his work.

A calorimetric method was employed: The energy absorbed by a reflection sample was determined from the rise in its temperature during irradiation. The radiation reflected at near-normal incidence was caught on a gold black absorber and its energy also determined calorimetrically. Measurements were made for the wavelength region of 0·35 μ to 4 μ or approximately the transmission limits of quartz. Filters were used to divide this region into bands. Measurements were made on Cu and Au samples prepared by electrolitic etching.

Table 6. Comparison of the Theoretical and Experimental Values of Absorptivity

Metal	Theory			Experimental
	Surface	Volume	Total	
Copper	0·0029	0·0020	0·0049	0·0050
Silver	0·0036	0·0009	0·0045	0·0044

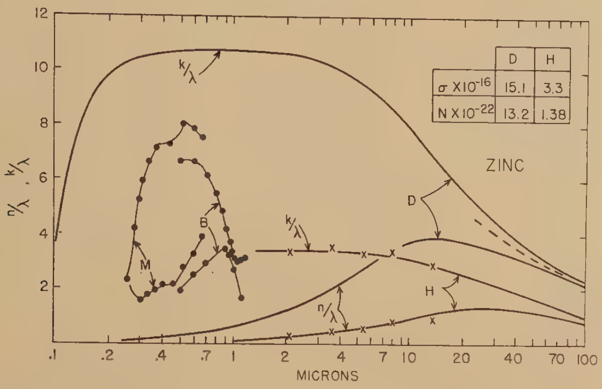
A summary of results obtained by Biondi for wavelengths greater than 1·5 μ is given in table 6. Recent theoretical work by Holstein (1954) has shown the need for dividing absorption into a volume and surface component as was done in the table. The most striking feature is the excellent agreement between the total predicted absorption and the actual experimental values. The experimental accuracy in A which is claimed seems somewhat too good in view of the difficulties in preparing the samples, but the calorimetric method does seem to be superior to the conventional optical methods.

7.5. *Multivalent Metals*

For multivalent metals the experimental investigations are not sufficiently complete to lead to definite conclusions. Consideration of Zn will illustrate the situation (Hagen and Rubens 1903, Meier 1910, Hodgson 1955, Bor *et al.* 1939, Graber 1925, Coblentz 1906, 1920, Bock 1945). In fig. 26 are shown the usual n/λ and k/λ curves calculated for a valence of two and also similar curves for an effective valence of 0·21 and a low value of σ, these latter values having been suggested by Hodgson (1955). Numerical values of σ and N are shown in the table where D refers to the usual Drude values and H to those of Hodgson. The experimental results of Meier (1910) and of Bor *et al.* (1939) for wavelengths less than 1 μ are grossly out of line with both the D and the

H curves. A surprising result is that the H curves suggest that the theory of the classical skin effect is not obeyed even at 100 μ. It may be that Hodgson's n values are too high which would lead to low calculated values of R_{air}. Accordingly various values for reflectivity will be compared.

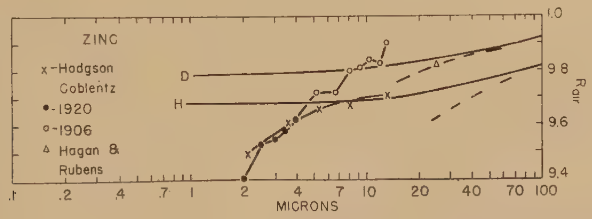
Fig. 26



Curves labelled D show n/λ and k/λ values calculated from the d.c. conductivity and an N value for a valence of two. Also shown are n/λ and k/λ curves labelled H for values of σ and N suggested by Hodgson (1955). Crosses (×) indicate Hodgson's experimental values; M refers to Meier (1910), and B to Bor *et al.* (1939).

The D and H values for reflectivity shown in fig. 27 were obtained by computation using n and k values given in fig. 26. Several sets of experimental values are indicated by appropriate symbols. The values of Coblentz (1906) seem to be close to the D curve but experimental uncertainties could be at least ±0·01, accordingly no definite conclusion can be drawn concerning the significance of his values. The same inconclusiveness applies to the one experimental point at 25·5 μ for Hagen and Rubens (1903) who claim to have verified the classical skin effect for Zn from this measurement. Because of these uncertainties in reflectivity measurements it is safest to conclude that Hodgson's n

Fig. 27

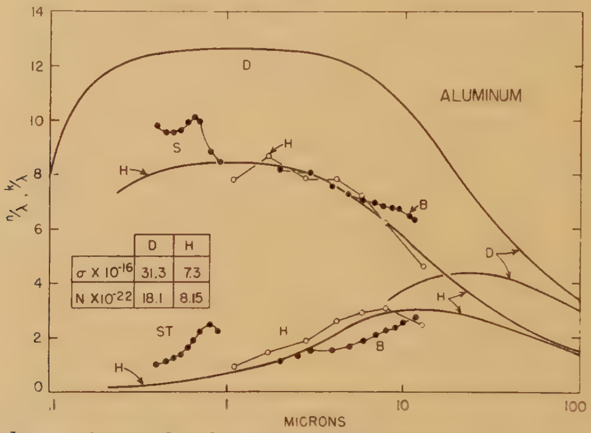


Reflectivity of Zn in air. Curves D and H show values computed for the n and k values in fig. 26. Experimental values are from Hodgson (1955); Coblentz (1906, 1920); and Hagen and Rubens (1903).

values may be too high and therefore the H value for σ in the table of fig. 26 may be too low. On the other hand his k values may be more nearly correct. Hodgson has pointed out that his N value (which is closely related to k values) is in agreement with a prediction made by Wilson (1936).

Aluminium, an example of a trivalent metal, is similar to the metals of the monovalent group Ag, Au, and Cu in many of its physical properties. Its widespread use as a mirror material makes it of great practical interest (Strong 1938); therefore, n and k values for Al have been included in table 5 (Schulz and Tangherlini 1954, Schulz 1954 a). A careful search for the optimum conditions for producing good Al films has been made by Hass (1946, 1955, 1956).

Fig. 28



Calculated and experimental values for $n\lambda$ and $k\lambda$ for Al. The symbols have the following meanings: B, Beattie (1955); H, Hodgson (1955); ST, Schulz and Tangherlini (1954); and S, Schulz (1954 a).

In fig. 28 are shown the usual n/λ and k/λ curves for a valence of three and in addition curves calculated from a set of values for σ and N given by Hodgson (1955). Between 1 and 10 μ the experimental values for k of Hodgson and of Beattie (1955) are in reasonable agreement. For the number of electrons per atom Hodgson suggests a value of 1·35 and Beattie and Conn a value of 1·28. In the range of 0·4 μ to 0·9 μ the experimental results (Schulz and Tangherlini 1954, Schulz 1954 a) do not agree with either set of values for σ and N. An objection to the results of Hodgson and of Beattie is that, as was the case for Zn, they lead to a departure from the classical skin effect theory in the far infra-red at 100 μ. Although more data are required to give a final conclusion, it appears that Al departs from the Drude theory at all wavelengths.

There is a great mass of experimental data (International Critical Tables 1926) for other metals, but much of it is of questionable accuracy and is confined to a limited wavelength range. Because these data are difficult to evaluate, they will not be examined in detail.

§ 8. CONCLUSIONS

The experimental results will be discussed in relation to the two general goals which were : First, determination of the range of validity of the Drude theory ; and second, discovery of information of use to solid state physics.

Examples have been given for each of the four degrees of agreement (discussed in § 2) between experimental results and the Drude theory of eqns. (4)–(6). (1) Liquid Hg and Ga illustrate complete agreement—in fact, the agreement is surprisingly good. (2) For wavelengths longer than $2\,\mu$ solid Ag and Au with m^* equal to m show good agreement. (3) For solid Cu, however, agreement results only for m^*/m equal to 1·45. (4) The liquid alloys (Hg–In) and (Hg–Tl) illustrate the case of no agreement with the Drude theory. The experimental results obtained by Beattie and by Hodgson for Al can be fitted rather well to an empirical value for σ as well as for N. (The use of σ as an adjustable parameter was rejected earlier when formulating the degrees of agreement.) Use of a low value of σ for Al is extremely difficult to understand since it requires abandoning the validity of the classical skin effect at wavelengths in the neighbourhood of $100\,\mu$ and longer. A possible explanation is that the current carriers are appreciably different from the conduction electrons of monovalent metals, but this is unlikely to be the case for a good conductor such as Al. Roberts (1955) has pointed out the possibility of explaining existing experimental results for a number of metals as absorption by several types of conduction electrons. It appears that the explanation of the optical properties of metals such as Al and Zn must be deferred until additional measurements are made.

Specific information of interest to solid state physics (the second goal) are the m^*/m values shown in table 4. This information would be more meaningful if an independent determination of either m^* or N could be made. At present this is possible only for semiconductors, and preliminary results (Spitzer 1956) show the usefulness of the Drude theory for studying optical phenomena in this type of solid. Of greater interest than any specific result is the more general one that the simple free electron theory as applied to optical properties of metals is quantitatively correct. This result is somewhat unexpected and calls for an explanation ; however, the existing theory which might be used is for the most part specifically for solids. The problem here includes the case of liquids as well for which there is practically no theory. Any thorough examination of the difficulties in explaining the experimental results is beyond the scope of this paper.

The usefulness of the simple Drude theory together with the success of absorption methods in all branches of physical science suggests the possibility of the 'absorption spectroscopy of metals' ; however, a difficulty is at once apparent. In the infra-red spectroscopy of organic compounds there are rather distinct absorption bands for each mechanism of absorption. For metals, on the other hand, the various mechanisms are not confined to bands but tend to be widespread and to overlap. Thus for Ag the minimum in the experimental value of k/λ at 0·32 in fig. 23 must be the super position of the absorption by conduction electrons on some other mechanism of absorption. At this point it is not known whether several modes of absorption are independent or whether they interact.

Concerning future experimental work it appears that there remains a need for accurate measurements in all wavelength ranges for nearly all metallic materials. At the present time the greatest need is probably for experimental work in the infra-red. The measurements of Beattie and Conn (1955) and of Hodgson (1955) although helpful need to be repeated with improved accuracy. It also would be worthwhile to develop better experimental methods as there are apparently difficulties with the polarizing spectrometer in the infra-red. With better methods and better samples one might hope for the accurate measurements which will provide the basis for the development of theories concerning absorption other than that by conduction electrons.

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